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**THE JOURNAL**  
**—OF THE—**  
**AMERICAN CHEMICAL SOCIETY.**

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**VOLUME XIX.**

**1897.**

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**COMMITTEE ON PAPERS AND PUBLICATIONS:**

**EDWARD HART, Editor,**

**J. H. LONG,**

**THOMAS B. OSBORNE.**

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# THE JOURNAL

## AMERICAN CHEMICAL SOCIETY.

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### THE PROPORTIONS OF CHLORINE AND OF NITROGEN AS NITRIC ACID AND AS AMMONIA IN CERTAIN TROPICAL RAIN-WATERS.

BY J. B. HARRISON AND JOHN WILLIAMS.

Received November 1, 1896.

**D**URING the years 1880 to 1885 determinations of the quantity of nitrogen present in the forms of nitric acid and ammonia were, from time to time, made by one of us upon samples of rain water which had fallen in the island of Barbados, British West Indies, and in others of the West Indian Islands.

It was noticed that the proportions of combined nitrogen present in the rain waters in the forms of nitric acid and ammonia did not in any way support the received ideas that tropical rain-water contains considerably higher proportions of combined nitrogen than does that of temperate climates.

When a Botanic Station was started in the island of Barbados, at Dodd's Reformatory, steps were taken to systematically collect samples of rain-water, representative of the whole rainfall. The samples were collected by J. R. Bovell, Esq., F.C.S., F.L.S., the superintendent of the Botanic Station, and analyzed as soon as possible after collection by one of us (J. B. H.). This was continued from June, 1885, to February, 1890, soon after the analyst was transferred to British Guiana.

In the latter colony, in January, 1890, steps were taken to carry out a similar investigation and samples representative of the whole rainfall were collected at the Government Laboratory and at the Botanic Gardens in Georgetown. The results reported in this paper are those obtained in Barbados in latitude

13° 4', north, and longitude 59° 37' west, during a period of four years and nine months, ended in February, 1890, and in Georgetown, Demerara, in latitude 6° 49' 24" north, and longitude 58° 11' 30" west, from January, 1890, to June, 1896, a period of six and a half years.

The investigation has therefore extended over a period of eleven years—long enough, we think, to supply a fairly reliable record of the contents in combined nitrogen of the rain-waters in these low latitudes.

Both in Barbados and at the Government Laboratory in British Guiana, the rain has been invariably collected by means of large (eight to ten inch) glass funnels fitted with 100 mesh wire gauze sieves to prevent the entrance, into the collecting vessel, of leaves, insects, etc.

At the Botanic Gardens, British Guiana, at the commencement of the investigation there, the rain was collected in an eight-inch copper rain gauge, later in both this and in a glass funnel, and finally by means of the glass funnel only.

From the commencement of the experiments the methods of analysis used have been but slightly varied. The chlorine has been always determined by direct titration with centinormal silver nitrate solution, standardized in solutions of sodium chloride of approximately the same strength as the rain-waters to be examined, using 100 cc. of the rain-water at each estimation.

During the first four years, the ammoniacal nitrogen was determined directly on the water by means of Nessler's test; a quantity of the water was made very faintly acid with oxalic acid specially purified from all traces of ammonia and nitrates, divided into two portions, one of which was allowed to act for two or three days until reduction of the nitrates was complete, upon zinc copper couples prepared as directed by M. W. Williams,<sup>1</sup> the other being kept for the purpose of diluting the standard ammonia solution used for comparison in nesslerizing the water which had been exposed to the action of zinc copper couples. The errors thus fell on the nitric nitrogen, but as the proportions of this in the rainfall under consideration was, as a rule, much higher than that of the ammoniacal nitrogen, the amount of error introduced would be small.

Since the publication of Warrington's paper<sup>2</sup> the ammoniacal

<sup>1</sup> Trans. Chem. Soc., 1881, 100.

<sup>2</sup> J. Chem. Soc., 55, 1889, 537.

and nitric nitrogen have been invariably determined by the method there given ; 500 cc. of the rain-water are boiled rapidly in a Keene's revenue still with a little recently ignited magnesia, or with a very minute amount of chemically pure sodium hydroxide prepared from sodium, until 200 cc. have distilled over. In an aliquot part of the distillate the ammonia is determined by nesslerizing. The residue in the flask of the still is transferred to a wide-mouthed stoppered bottle containing copper zinc couples and kept closely stoppered at the temperature of the laboratory, 25° to 30° C., for four or five days. The water is afterwards distilled and the ammonia in the distillate, representing the nitrogen originally present as nitric acid, determined. Traces only of nitrites in a few instances have been detected in the rain-waters.

During this investigation 306 samples, representing the whole rainfall, have been examined.

Fortnightly and frequently weekly examinations were made of the rainfall during the first eight years of the experiments, but since 1893 monthly examinations only have been made of the mixed rain-water collected during the month.

#### BARBADOS RAIN.

The average compositions of the yearly rainfalls are shown in the following :

Years.	1885. Seven months.	1886.	1887.	1888.	1889.
Inches of rain .....	34.65	74.50	59.52	55.77	66.11
No. of samples analyzed	22	36	44	38	53
Milligrams per liter at 27° C.					
Chlorine .....	7.755	7.604	8.417	8.473	7.923
Nitrogen as nitric acid.	0.097	0.255	0.173	0.153	0.200
Nitrogen as ammonia..	0.116	0.070	0.076	0.046	0.082
Pounds per acre.					
Chlorine .....	60.850	128.300	113.450	107.010	118.611
Nitrogen as nitric acid.	0.761	4.302	2.332	1.932	2.994
Nitrogen as ammonia..	0.910	1.181	1.024	0.581	1.228

The average compositions of the monthly rainfalls and of the wet and dry seasons were as follows :

Months and seasons.	No. of years.	No. of samples analyzed	Average rainfall in inches	Mgms. per liter at 27° C.			Pounds per acre.		
				Chlorine.	Nitrogen as nitric acid.	ammo- nia.	Chlorine.	Nitrogen as nitric acid.	ammo- nia.
January..	4	14	2.94	14.171	0.160	0.074	9.435	0.106	0.049
February.	4	13	2.03	21.514	0.195	0.093	9.890	0.089	0.043
March ...	4	11	1.66	17.796	0.240	0.124	6.691	0.090	0.046
April ....	4	10	1.17	16.818	0.346	0.161	4.457	0.092	0.042
May .....	5	13	3.65	8.706	0.226	0.068	7.181	0.187	0.056
June .....	5	18	4.49	9.489	0.161	0.069	9.648	0.163	0.070
July .....	5	21	6.98	7.479	0.170	0.094	11.822	0.268	0.148
August...	5	21	10.12	6.388	0.155	0.091	14.640	0.355	0.208
Sept'mber	5	19	8.00	5.838	0.103	0.061	10.574	0.186	0.110
October ..	5	20	5.56	5.904	0.161	0.073	7.468	0.203	0.092
November	5	20	8.19	5.422	0.233	0.051	10.056	0.442	0.094
December	5	13	4.61	9.977	0.263	0.048	10.416	0.275	0.050
Wet season July to November.		101	38.85	6.197	0.164	0.074	54.520	1.443	0.651
Dry season December to June.		92	20.55	13.422	0.215	0.077	62.461	1.000	0.358

Wide variations occurred in both the chlorine and nitrogen contents of different rainfalls. The samples which were examined during the investigation which had the highest and lowest contents showed as follows :

	Mgms. per liter.	
	Highest.	Lowest.
Chlorine .....	47.042	2.476
Nitrogen as nitric acid.....	0.914	0.001
Nitrogen as ammonia .....	1.812	none

The average annual rainfall during these experiments was at the rate of 59.40 inches, having as average contents in milligrams per liter at 27° C., 8.699 of chlorine, 0.181 of nitrogen as nitric acid, and 0.075 of nitrogen as ammonia, and yielding to the soil 116.98 pounds of chlorine, 2.443 pounds of nitric nitrogen, and 1.009 pounds of ammoniacal nitrogen per acre. Of these approximately two-thirds of the ammoniacal nitrogen and three-fifths of the nitric nitrogen were contained in the rain which fell in the five months comprising the rainy season, during which period electrical atmospheric disturbances are common in Barbados.

In 1886, on August 16, an opportunity occurred for the collection and examination of samples of the rain which fell whilst a hurricane was raging to the north of the island. 9.14 inches were collected and were found to contain



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	Mgms. per liter.
Chlorine .....	42.52
Nitrogen as nitric acid.....	0.329
Nitrogen as ammonia.....	0.057

The rain of this storm supplied 0.681 pounds of nitrogen as nitric acid per acre, or equal to twenty-eight per cent. of the average amount present in an ordinary year's rainfall.

BRITISH GUIANA RAIN.

The average compositions of the yearly rainfalls collected in this colony are shown in the following :

Years.	1890.	1891.	1892.	1893.	1894.	1895.	1896. Eight months.
Inches of rain .....	125.63	109.38	128.03	135.24	76.67	82.56	64.55
No. samples analyzed	39	26	24	12	12	12	8
	Mgms. per liter at 27° C.						
Chlorine.....	8.293	5.284	3.827	3.155	3.032	4.187	5.179
Nitrogen as nitric acid	0.090	0.128	0.035	0.066	0.036	0.237	0.082
Nitrogen as ammonia	0.075	0.034	0.043	0.068	0.045	0.065	0.078
	Pounds per acre.						
Chlorine.....	235.780	130.900	110.595	96.600	52.640	78.280	78.710
Nitrogen as nitric acid	2.559	3.171	1.015	2.022	0.625	4.431	1.199
Nitrogen as ammonia.	2.135	0.842	1.247	2.083	0.781	1.215	1.141

The average compositions of the monthly rainfalls and of the wet and dry seasons were as follows :

Months and seasons.	No. of years.	No. of samples analyzed	Average rainfall in inches	Mgms. per liter at 27° C.			Pounds per acre.		
				Chlorine.	Nitrogen as nitric acid.	ammo- nia.	Chlorine.	Nitrogen as nitric acid.	ammo- nia.
January..	7	11	13.21	6.174	0.097	0.030	18.469	0.290	0.090
February.	7	13	10.19	6.417	0.102	0.060	14.808	0.235	0.138
March ...	7	13	7.26	5.043	0.063	0.100	8.291	0.103	0.164
April ....	7	14	8.05	6.197	0.087	0.094	11.297	0.158	0.171
May .....	7	12	12.29	5.595	0.086	0.062	15.572	0.239	0.173
June .....	7	13	12.93	3.278	0.104	0.033	9.598	0.304	0.096
July .....	7	12	10.96	3.076	0.116	0.038	7.634	0.288	0.094
August...	7	12	6.81	3.399	0.089	0.111	5.242	0.137	0.171
Sept'mber	6	9	2.50	4.846	0.119	0.014	2.743	0.067	0.008
October ..	6	8	1.99	7.113	0.120	0.142	3.205	0.054	0.064
November	6	8	5.58	4.001	0.121	0.121	5.056	0.153	0.153
December	6	10	14.94	3.321	0.049	0.023	11.236	0.165	0.078
Wet seasons December to February. May to July.	71		74.52	4.313	0.090	0.039	72.784	1.519	0.658
Dry seasons March and April. August to November.	64		32.19	4.915	0.092	0.091	35.829	0.671	0.663

During the period over which the experiments have been

spread, the rainfall has been at an average rate of 106.71 inches per annum and has contained 4.494 mgms. of chlorine, 0.0915 mgm. of nitric nitrogen and 0.055 mgm. of ammoniacal nitrogen per liter at 27° C. This is equivalent to a yield of 108.613 pounds of chlorine, 2.190 pounds of nitric nitrogen, and 1.351 pounds of ammoniacal nitrogen per acre.

During this part of the investigation the highest recorded contents of chlorine was 16.10, the lowest 0.45 mgm. per liter. The highest contents of nitric nitrogen was 0.823 and of ammoniacal nitrogen 1.376 mgms. per liter; the lowest in both cases was none.

#### THE INFLUENCE OF THE COLLECTING VESSEL UPON THE APPARENT COMPOSITION OF THE RAIN.

At the commencement of the investigation in British Guiana, samples were collected in the grounds of the Government Laboratory by means of a glass funnel and at the Botanic Gardens by means of an eight-inch rain gauge. It was at once noticed that the rain collected in the metal gauge invariably contained the higher proportions of ammoniacal nitrogen and usually also of nitric nitrogen. In consequence a glass funnel was afterwards used at the Botanic Gardens being placed on the tower of the house some fifty feet above the ground. During the latter half of 1890 determinations were regularly made of the contents of nitric and ammoniacal nitrogen in the rain collected by the two receivers. The following gives in mgms. per liter at 27° C. the results obtained from June to December, 1890:

Month.	Inches of rain.	Collected by glass funnel.		Collected by metal gauge.	
		Nitrogen as nitric acid.	ammonia.	Nitrogen as nitric acid.	ammonia.
June.....	13.17	0.087	0.123	0.352	1.860
July .....	10.90	0.225	0.046	0.723	3.257
August ....	5.71	0.075	0.270	0.486	4.000
September.	3.18	0.263	0.026	3.047	1.138
October....	0.16	0.823	0.296	0.626	1.057
November .	2.97	0.214	0.091		
December .	9.47	0.049	0.015	0.330	0.178

The rainfall amounted to 45.56 inches in the six months and whilst the rain collected by the glass funnel contained an average of 0.125 mgm. per liter of nitric nitrogen and 0.092 of ammoniacal nitrogen that collected in the rain gauge contained 0.660

and 2.007 mgms. per liter of nitric and ammoniacal nitrogen respectively. Examinations of the rain collected in the rain gauge showed that it usually contained phosphoric acid and that the high content of nitrogen, which might have been considered as characteristic of tropical rain, was due to contamination of the receiving surface by birds. It was noticed that birds, in which this colony is peculiarly rich, constantly frequented and perched upon the copper gauge whilst they avoided the glass funnel, scared, probably, by the reflected rays of the sun.

To further examine into this matter, in 1892, determinations were made on the rains collected in a small copper rain gauge and by a glass funnel in the grounds of the Government Laboratory. These were placed side by side, about twelve inches apart, at about three feet above the ground so as to avoid splashing from the soil, as it was probably to nitrification induced by such splashing that the high content of nitric nitrogen noticed in the rain collected in the Botanic Garden's rain gauge was due. The following are the results in mgms. per liter, at 27° C., of the comparisons made during the months of July, August, and September, 1892 :

Month.	Inches of rain.	Collected by glass funnel.		Collected in metal gauge.	
		Nitrogen as nitric acid.	ammonia.	Nitrogen as nitric acid.	ammonia.
July . . . . .	11.40	0.051	0.063	0.037	0.229
August . . . .	8.05	0.053	0.222	0.049	0.652
September.	5.78	0.060	0.007	0.126	2.751

The rainfall of 25.24 inches contained 0.053 and 0.100 mgm. per liter, respectively, of nitric and ammoniacal nitrogen when collected by the glass funnel and 0.061 and 0.942, respectively, when collected in the copper gauge. Here, where there was but little chance of nitrification being induced by splashing from the earth, it is evident that the excess of nitrogen in the water collected by the copper rain gauge, was almost entirely in the form of ammonia. We are desirous of placing these observations on record, as they may to some extent explain the high nitrogen contents reported at times in the tropical rain-waters by other observers.

In our results, as far as used for the determination of the nitrogen present as nitric acid and ammonia we have, of course, only taken into consideration the figures obtained from the examinations of rain collected by means of glass funnels.

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### COMPARISON OF THE RESULTS OBTAINED IN BARBADOS AND BRITISH GUIANA WITH THOSE REPORTED FROM ELSE- WHERE.

With an average annual rainfall in Barbados of 59.40 inches, the rain contained 0.101 mgm. per liter of nitrogen as nitric acid and 0.075 mgm. per liter of nitrogen as ammonia. The average amount of nitrogen in the two forms was therefore equal to 3.452 pounds per acre per annum.

With an average annual rainfall in British Guiana of 106.71 inches, the rain contained 0.0915 mgm. of nitrogen as nitric acid and 0.055 mgm. of nitrogen as ammonia per liter, at 27° C. Thus, the average amount of nitrogen in these two forms was equal to 3.541 pounds per acre per annum.

We may safely assume, therefore, that during the eleven years over which the investigation has extended, the nitrogen contents of the rainfall present as nitric acid and ammonia was approximately three and a half pounds per acre per annum in these two colonies situated in the tropics and in the direct course of the trade-winds.

The total amount of nitrogen present in the Rothamsted rain-water is given by Warrington,<sup>1</sup> at 3.74 pounds per acre per annum, a figure with which our results obtained by similar methods of analysis closely agree.

The Barbados rain-water contained approximately three-fourths of the nitrogen as nitric nitrogen; the British Guiana rain-water, two-thirds of the nitrogen as nitric nitrogen; while in the Rothamsted rain-water the nitric nitrogen was approximately only one-fourth of the whole.

Results obtained in New Zealand and at Tokio, in Japan, quoted by Warrington in his paper, show decidedly lower contents of nitrogen in these forms; and in both of these places the ammoniacal nitrogen is present in the rain water in far higher proportions to the nitric nitrogen than we have found here in the tropics. It is probable, therefore, that the rain-water of the tropics contains a higher proportion of its nitrogen present as nitric acid than does that of temperate climates.

As regards tropical rain, the only published results we are acquainted with are those of Müntz and Marcano,<sup>2</sup> on rain-waters

<sup>1</sup> *Loc. cit.*

<sup>2</sup> *Compt. rend.*, 108, 1062.

from Caracas, Venezuela, and from St. Denis, Reunion. In the former the mean proportion of nitric nitrogen was found to be 0.578 part per million, in the latter 0.69 part.

These results are far in excess of the quantities found by us, although, from time to time, instances have occurred to us in which the nitrogen present as nitric acid has approached or even exceeded these amounts.

Possibly, the results obtained by Müntz and Marcano were from rainfalls lower in quantity than those which occurred during our present investigation, whilst probably the composition of rain-water may be materially affected by the prevalence or not of the trade-winds.

Briefly our somewhat extended investigation leads to the conclusion that the rainfalls of certain tropical climates whilst containing a higher relative proportion of the nitrogen as nitric acid, do not supply to the soil a larger quantity of nitrogen as nitric acid and as ammonia than is supplied by the rain-water of temperate climates.

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## ANALYSIS OF AN IRON RAIL TAKEN FROM A GALLERY OF AN UNUSED COAL MINE.

BY H. P. TALBOT AND A. G. WOODMAN.

Received November 21, 1896.

THE section of the rail in question was taken from a gallery of the "Hub Mine," at Glace Bay, Cape Breton. The gallery was allowed to fill with water in 1872, and was pumped out by the Dominion Coal Company last year. The rail had, therefore, lain unused in the gallery for over twenty years, most of the time under water which is reported to be "impregnated with acid," and, as indicated by the analysis, had undergone an entire change in composition. The rail was initially, presumably, of cast iron, and it is interesting to record the report which has come to us, that utensils of steel, and articles of wrought iron, did not undergo material change during the same length of exposure to the same conditions. So far, the writers have not had opportunity of examining any of these samples of wrought iron or steel.

After the mine had been pumped out, the rail was found to have lost its initial density and strength, and was easily broken or cut into fragments.

In the sample which came into our possession, there was a well-defined demarcation between the inner core, which was gray and very soft, and the outer shell, which was black and relatively hard, although this too could be readily cut with a knife and powdered in a mortar. The two portions were easily separated by running a knife blade along the line of demarcation. The outer and inner portions were examined separately.

Before presenting the results, the writers wish to state that the analytical work has been done at irregular intervals, and that the results are given solely for the interest which the figures seem to possess in themselves, and with the consciousness that, considered as an investigation, the report would be incomplete.<sup>1</sup>

The results are as follows :

	Outer shell.	Inner core.
Specific gravity (compared with water at about 20° C.) .....	2.45	2.16
	Per cent.	Per cent.
Lost on ignition at a red heat .....	7.50	8.75
Total iron .....	42.00	38.10
Total silicon .....	5.85	10.60
Total phosphorus .....	3.60	3.75
Sulphur evolved by treatment with acid.	2.30	0.73
Sulphur in the residue after evolution method .....	2.35	0.68
Carbon corresponding to graphitic carbon	9.50	16.00

Manganese and aluminum were present in very small quantities. The former could not be precipitated in weighable quantities, except by using so large a sample that determination was not attempted.

No silicon, as such, was detected by ignition of the sample in dry chlorine. The presence of metallic iron was plainly indicated by the deposition of metallic copper, when fragments of the rail were placed in copper sulphate solution. The amount is distinctly larger in the outer shell than in the inner core. During solution in acids, a distinct odor of hydrocarbons was detected, but a combustion of the residue after treatment with copper potassium chloride, yielded a lower percentage of carbon

<sup>1</sup> Shortly after the transmission of the manuscript of this paper to the editor, a detailed description of the properties and analysis of other specimens from the same source, by F. W. Durkee, appeared in the *Am. Chem. J.*, 18, 549. Interesting information concerning the mine-water, and the possible steps in the transformation of the iron, are also presented.

than was found in the residue after treatment with nitric acid (as given above). This may possibly be explained by the incomplete decomposition of the substance by the copper-ammonium salt, with the consequent protection of some of the carbonaceous by the mineral matter.

The loss on ignition at a red heat does not probably represent any definite quantity, but is given as having some possible interest.

The statement was made to us by one who had had opportunity to handle a fragment of the rail of considerable size, and during an interval of a year or more, that its density perceptibly increased with length of exposure to the air. The determinations of specific gravity already cited, were made about April 15, 1896. New determinations, made November 14, gave as results, for the outer shell 2.83, and for the inner core 2.23. While these results confirm the general statement, we do not feel that they are above criticism, as they were obtained from small fragments. They are comparable, however, with the earlier specific gravity determinations.

In connection with the foregoing statements, it is interesting to note the results reported by Herting,<sup>1</sup> of an analysis of a similar fragment of rail, which not improbably came from the same source, as he mentions it as coming from a mine in Cape Breton, in which the rail had remained for twenty years. His results are as follows :

Specific gravity, 2.053 ; silicon, 14.20 per cent. ; graphitic carbon, 24.20 per cent. ; phosphorus, 5.85 per cent. ; total sulphur, 1.00 per cent. ; manganese, 1.93 per cent. ; iron, metallic, 31.50 per cent.

He finds that approximately one-half of the sulphur is volatile with acids, as in the results cited in this paper, and considers that the iron is otherwise present as  $\text{Fe}_2\text{O}_3$ . His percentages, upon recalculation, yielded the following : Ferrous sulphide, 1.37 per cent. ; ferrous sulphate, 2.38 per cent. ; manganese monoxide, 2.50 per cent. ; phosphorus pentoxide, 13.37 per cent. ; magnetic oxide ( $\text{Fe}_3\text{O}_4$ ), 39.34 per cent., which with the carbon and silicon, yields a total of 97.36 per cent. It would appear, however, from our results, that the silicon was probably present as silica in his samples as well, at least in some measure.

<sup>1</sup> *Chem. Ztg.*, 20, 54.

Our analytical examination has not been, and cannot well be continued further than to afford the results cited above; hence we prefer not to express a positive opinion as to the probable combinations of the constituents as they occur in the rail, nor do we feel able to offer any explanation as to how the changes in composition have been brought about. Merely for comparison with Herting's results, we present our own, calculated upon the same basis, except that the silicon is calculated as oxide.

They are as follows:

	Outer shell. Per cent.	Inner core. Per cent.
Carbon .....	9.50	16.00
Silica.....	12.45	22.55
Phosphoric anhydride .....	8.25	8.60
Ferrous sulphide.....	6.30	2.00
Ferrous sulphate.....	11.15	3.20
Magnetic oxide ( $\text{Fe}_3\text{O}_4$ ).....	46.80	49.20

The writers wish to express their obligations to Mr. J. B. Dillingham, and Prof. W. H. Niles, through whose courtesy they came into possession of the fragment of the rail, and to whom they are indebted for information as to its history.

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[CONTRIBUTIONS TO THE CHEMISTRY OF ZIRCONIUM, No. 6.]

## THE OXALATES OF ZIRCONIUM.

BY F. P. VENABLE AND CHARLES BASKERVILLE.

Received November 30, 1896.

THE text-books of chemistry make either very little or no reference to the oxalates of zirconium. Beyond an occasional reference to the oxalate or basic oxalate gotten by precipitating with oxalic acid or an oxalate, we can find little mention of these compounds. Behrens, in his microchemical work, speaks of an oxalate prepared as colorless pyramids by precipitating a solution of zirconium sulphate with potassium binoxalate, but no analyses are given, and the crystals could scarcely have been the pure oxalate. Paykull<sup>1</sup> speaks of double oxalates being prepared with the alkaline oxalates (1:2) and of his failure to prepare the neutral oxalate. His methods, and indeed full results, are unknown to us, as we did not have access to the original paper.

We may summarize the work which follows in the succeeding pages by saying that we found it possible to prepare the basic oxalates by precipitation. This was usually in the form of

<sup>1</sup> Ofv. af. Vet. Ak. Förhandl. ref. in *Ber. d. Chem., Ges.*, 12, 1719.



$\text{Zr}(\text{C}_2\text{O}_4)_2 \cdot \text{Zr}(\text{OH})_2$ , though other ratios were gotten. The neutral oxalate we did not succeed in preparing, but instead the tendency seems to be toward the formation of the acid oxalate,  $\text{Zr}(\text{C}_2\text{O}_4)_2 \cdot \text{H}_2\text{C}_2\text{O}_4 \cdot 8\text{H}_2\text{O}$ . This tendency toward the formation of acid salts was shown also in the double oxalates. Two of these were prepared. For sodium,  $\text{Zr}(\text{C}_2\text{O}_4)_2 \cdot 3\text{Na}_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{C}_2\text{O}_4 \cdot 5\text{H}_2\text{O}$ , and for potassium the salt  $[\text{Zr}(\text{C}_2\text{O}_4)_2] \cdot (\text{K}_2\text{C}_2\text{O}_4)_2 \cdot \text{H}_2\text{C}_2\text{O}_4 \cdot 8\text{H}_2\text{O}$ . The oxalate with ammonium as a constituent was not so easy of preparation in a pure state. The compound secured was  $\text{Zr}(\text{C}_2\text{O}_4)_2 \cdot 2(\text{NH}_4)_2\text{C}_2\text{O}_4$ . The experiments and analyses are given in detail.

#### ZIRCONIUM OXALATES.

*The Oxalate Gotten by Precipitation.*—On the addition of a saturated solution of oxalic acid to a slightly acid solution of zirconium chloride until no further precipitation occurred, a gelatinous precipitate formed which had very nearly the composition  $\text{Zr}(\text{C}_2\text{O}_4)_2 \cdot 2\text{Zr}(\text{OH})_2$ . Analysis I gave Zr, 46.39, and  $\text{C}_2\text{O}_4$ , 30.89, instead of the theoretical 46.40 and 30.93 respectively. The filtrate from this was turbid, and on standing yielded another precipitate which had nearly the composition  $2\text{Zr}(\text{C}_2\text{O}_4)_2 \cdot 3\text{Zr}(\text{OH})_2$ .

These basic oxalates are very difficultly soluble in acids, and of extremely fine subdivision, settling slowly and passing through even the best filters. It does not seem probable that they could be secured of very constant composition. Probably basic oxalates with many different ratios between the oxalate and the hydroxide might be secured. On drying at  $100^\circ$ , or even a little lower, the oxalic acid is gradually volatilized and lost. This is true of all the oxalates and double oxalates prepared so that the only mode of drying these preparations was between filter paper.

*The Acid Oxalate Prepared by Crystallization.*—In preparing this oxalate, zirconium hydroxide was dissolved in oxalic acid. The hydroxide is quite soluble in oxalic acid, and a concentrated solution is readily obtained. A considerable excess of the acid is required to hold the oxalate thus formed in solution. If this solution be acidified by means of hydrochloric acid a very fine precipitate is obtained settling very slowly, easily passing through the best filter papers and insoluble even in a considera-

ble excess of the acid, but soluble in concentrated sulphuric acid. This precipitate was not analyzed, nor were the exact conditions of its formation determined, as its examination did not promise results of sufficient importance to justify overcoming the difficulties in the way.

On evaporating the acid solution of the oxalate the excess of oxalic acid first crystallized out. In the various preparations made, the first one or two crops of long crystals were found to be nearly pure oxalic acid, and were rejected. Then the form of the crystals changed to small granular or prismatic masses, and with each succeeding crop of crystals the percentage of zirconium increased, reaching speedily an approximately constant ratio. No difference in the form of the crystals in these different crops could be detected on superficial examination, and hence it was impossible to distinguish between the zirconium oxalate and the oxalic acid almost free of zirconium, except by analysis. In no case was the normal oxalate secured. The analyses showed a tendency toward the formation of an acid oxalate and to mixtures of this with the normal oxalate. These mixtures were gotten in the later crystallizations, but the last crystallization, when nearly the whole would solidify into a crystalline mass, showed decreased percentages of zirconium. It is possible that larger amounts than we had at our disposal would enable one to so fraction the crystallizations as to secure a pure oxalate. It is, however, questionable whether the normal oxalate can exist in solution without admixture with some oxalic acid.

Four series of crystallizations were made, and in two cases fairly abundant crops of crystals corresponding to the acid oxalate were obtained. In each series enough of the zirconium hydroxide was taken to form about twenty grams of the oxalate.

	First series. Sixth fraction. II.	Second series. Fifth fraction. IIL	$\text{Zr}(\text{C}_2\text{O}_4)_2 \cdot \text{H}_2\text{C}_2\text{O}_4$ .
Zr .....	25.44	25.28	25.53
$\text{C}_2\text{O}_4$ .....	74.55	74.72	74.47

These are calculated upon the water-free basis. The crystals contained 29.34 and 29.27 per cent. of water respectively, where the salt  $\text{Zr}(\text{C}_2\text{O}_4)_2 \cdot \text{H}_2\text{C}_2\text{O}_4 \cdot 8\text{H}_2\text{O}$  contains 28.90 per cent. Other crops of crystals contained percentages of zirconium not varying greatly from these given above as 28.14, 27.62, 24.9, 23.83.

The percentage of zirconium in the normal oxalate is 33.96.

#### ZIRCONIUM SODIUM OXALATE.

The addition of sodium oxalate to a slightly acid solution of zirconium chloride gives a gelatinous white precipitate. Most of this dissolves in an excess of the oxalate. The undissolved portion settles to the bottom, and after prolonged standing, a second layer of a more powdery appearance forms. This can also be gotten by concentration of the filtrate from the first precipitate. Analysis showed that the first gelatinous precipitate was chiefly  $\text{Zr}(\text{OH})_4$ . The second precipitate was a double oxalate of zirconium and sodium, but was either of inconstant composition (varying ratios of sodium to the zirconium), or was decomposed by the washing.

The analyses, calculated on a dry basis, gave:

	IV.	V.	VI.
Zr .....	53.12	46.86	41.98
Na .....	9.16	4.10	1.07
$\text{C}_2\text{O}_4$ .....	38.06	39.64	42.95

If the solution made with the excess of sodium oxalate was diluted considerably with water, a gelatinous precipitate was formed, very fine and insoluble. Precipitates were also formed by the addition of hydrochloric acid. This mode of forming the double oxalate was abandoned, and the following method was adopted with greater success. Zirconium hydroxide was dissolved in an excess of oxalic acid, and to this a concentrated solution of sodium hydroxide was added, bringing it nearly to neutralization. When the solution was concentrated an abundant crop of crystals was obtained on cooling, a good deal of heat being evolved in the mixing. Further evaporation yielded other crops of crystals. These were washed, dried between filter paper and analyzed. The results are given in the following table:

	VII.	VIII.	IX.	Calculated.
Na .....	18.14	17.46	17.75	18.19
Zr .....	12.59	12.66	12.78	11.93
$\text{C}_2\text{O}_4$ .....	69.27	66.89	69.47	69.88

These results show a somewhat wide variation from those calculated. This probably arises from the fact that the fractions were not composed of the crystals of a single kind of oxalate, but had other oxalates mixed with them in small amounts. Examined under a magnifying glass they seemed to be homo-

geneous, but the different crops could not be distinguished from one another. They were all small, hard prismatic crystals, somewhat difficultly soluble in water. One set of crystals, the analysis of which is reported under VII in the above table, was redissolved in water and recrystallized. On analysis it yielded the following results:

	VII.	XI.
Na .....	18.14	18.19
Zr .....	12.59	12.71
C <sub>2</sub> O <sub>4</sub> .....	69.27	69.10

These were calculated upon a water-free basis. The crystals from the various crops mentioned above did not contain a very constant amount of water, but ranged from 9.13 to 11.06. The calculated amount of water in  $\text{Zr}(\text{C}_2\text{O}_4)_3 \cdot 3\text{Na}_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{C}_2\text{O}_4 \cdot 5\text{H}_2\text{O}$  is 10.62. It would seem, therefore, that the tendency, when this method of formation is adopted, is toward the formation of crystals containing free oxalic acid and with the sodium and zirconium oxalates bearing a ratio of three to one.

#### ZIRCONIUM POTASSIUM OXALATE.

The curdy precipitate gotten by precipitating zirconium chloride with normal potassium oxalate is insoluble in an excess of either of the substances. The precipitate first obtained is an impure zirconium hydroxide, containing only small amounts of oxalic acid. The supernatant liquid on concentration yields needle-like crystals of potassium oxalate, carrying only traces of zirconium. After the separation of a good deal of this potassium oxalate, further concentration yielded a gelatinous substance having the composition (XII): Zr, 39.34; K, 5.06; C<sub>2</sub>O<sub>4</sub>, 43.05; which seems to be a basic zirconium oxalate, mixed or united with a small proportion of potassium oxalate. If the potassium be calculated as potassium oxalate and subtracted, the composition of the remainder would be approximately  $\text{Zr}(\text{OH})_2 \cdot \text{Zr}(\text{C}_2\text{O}_4)_3$ .

On adding potassium binoxalate to a solution of zirconium chloride a white curdy precipitate was obtained which was not completely soluble in excess of the binoxalate. The somewhat turbid solution was filtered and evaporated. Large crystals resembling those of oxalic acid formed. These were separated, and on analysis proved to be oxalic acid. At the same time a number of small crystals were formed, which were mechanically

separated, washed and dried. These were analyzed and are reported under XIII. A further crop was gotten from the mother liquor, and the analysis is given under XIV.

	XIII.	XIV.
Zr.....	19.59	17.99
K .....	16.18	13.91
C <sub>2</sub> O <sub>4</sub> .....	64.23	68.09

The curdy precipitate, which first formed, was also examined and found to have the composition  $\text{Zr}(\text{C}_2\text{O}_4)_3 \cdot 2\text{Zr}(\text{OH})_2$ .

The addition of a solution of potassium tetroxalate to zirconium chloride gave a gelatinous precipitate of zirconium oxalate (basic), carrying a little potassium oxalate. Subtracting the potassium oxalate, the percentages (XVI) Zr, 39.09 and C<sub>2</sub>O<sub>4</sub>, 38.63 are left, which are not very different from the figures gotten for the precipitate from potassium oxalate (neutral).

This curdy gelatinous precipitate was dissolved in excess of tetroxalate and the solution placed over sulphuric acid to crystallize, and yielded crystals having the composition (XVII): Zr, 20.85; K, 16.72; and C<sub>2</sub>O<sub>4</sub>, 62.31. As will be seen, these are not far from the 1 : 2 zirconium potassium oxalate, with excess of oxalic acid.

When potassium hydroxide was added to a solution of zirconium oxalate in oxalic acid until nearly neutral and then set aside for crystallization, various crops of crystals were gotten, as in the case of the double sodium oxalates. These crops of crystals were similar in appearance to the sodium crystals. They were analyzed and showed fairly constant composition.

	XVIII.	XIX.	XX.	XXI.	(Zr(C <sub>2</sub> O <sub>4</sub> ) <sub>3</sub> ) <sub>2</sub> · (K <sub>2</sub> C <sub>2</sub> O <sub>4</sub> ) <sub>3</sub> · H <sub>2</sub> C <sub>2</sub> O <sub>4</sub> · 8H <sub>2</sub> O.
Zr.....	18.08	19.25	19.83	18.47	18.95
K .....	16.41	16.35	14.84	14.46	16.34
C <sub>2</sub> O <sub>4</sub> .....	66.51	64.40	65.33	67.07	64.71

The three previous analyses may also be referred to here as having approximately the same composition. See Analyses XIII, XIV, XVII. These are calculated as water-free. In the Analyses XVIII and XIX the percentages of water were 12.99 and 12.38. These would correspond to the formula  $(\text{Zr}(\text{C}_2\text{O}_4)_3)_2 \cdot (\text{K}_2\text{C}_2\text{O}_4)_3 \cdot \text{H}_2\text{C}_2\text{O}_4 \cdot 8\text{H}_2\text{O}$ . In this case, as in the zirconium oxalates and the sodium oxalates, the crystals seem to form only along with free oxalic acid, giving acid salts.

#### ZIRCONIUM AMMONIUM OXALATES.

The addition of a solution of ammonium oxalate to the slightly acid solution of zirconium chloride gave a heavy gelatinous pre-

precipitate which was soluble in excess of ammonium oxalate and proved to be zirconium hydroxide with more or less zirconium oxalate and small amounts of ammonia. The filtrate from this precipitate was evaporated slowly and a fine crystalline powder obtained. This contained (XXII) Zr, 42.17 per cent. and  $C_2O_4$ , 39.86 per cent. This is in fair agreement with  $Zr(C_2O_4)_2 \cdot Zr(OH)_4$ . When ammonium oxalate is added until the first gelatinous precipitate is redissolved and then evaporated to crystallization, different crops of crystals can be gotten containing various amounts of ammonia. These did not seem to have any regular composition in our experiments and were looked upon as basic zirconium oxalates with varying amounts of ammonium oxalate present. Thus for one of these the figures (XVIII) Zr, 31.48;  $NH_3$ , 7.14; and  $C_2O_4$ , 61.38 were gotten.

Abandoning this method and using the one adopted in the cases of the sodium and potassium double oxalates, a more favorable result was obtained. Zirconium hydroxide was dissolved in excess of oxalic acid and then this was nearly neutralized by means of ammonium hydroxide. Analyses of these crops of crystals follow :

	XXIV.	XXV.	$Zr(C_2O_4)_2 \cdot 2(NH_4)_2C_2O_4$
Zr .....	16.55	16.66	17.58
$NH_3$ .....	14.46	13.35	13.28
$C_2O_4$ .....	69.99	69.99	68.94

While these do not show that the crystals had been thoroughly purified, the results indicate that the composition is one zirconium oxalate to two ammonium oxalate. On recrystallizing one of these crops of crystals, zirconium hydroxide was observed to separate when the solution was heated (to evaporate to crystallization), and the crystals which were obtained consisted of ammonium oxalate alone.

In general it may be stated that the zirconium oxalate fails to show any decided tendency to enter into clearly defined combinations with the alkaline oxalates, exhibiting rather a power of crystallizing along with them in mixtures of any proportions. It can only be said at best that under the conditions of our experiments certain ratios seem to be preferred, and appeared more persistently. In all cases the crystals formed from oxalic acid solutions, and this free oxalic acid crystallized with them, giving acid oxalates.

[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF THE U. S. DEPARTMENT OF AGRICULTURE, No. 23.]

## THE MECHANICAL ANALYSIS OF BASIC PHOSPHATIC SLAGS.

BY H. W. WILEY.

Received November 25, 1896.

**B**EFORE discussing the subject matter of the paper which I now present, I think it desirable to give a short sketch of the earlier literature relating to basic slags and the methods of their valuation.

In 1882, while examining some very finely ground bone in the Laboratory at Purdue University, Lafayette, Indiana, I noticed a marked solubility of the phosphoric acid therein in neutral citrate of ammonia. At that time Mr. H. A. Huston, who was a student in my laboratory, was directed to make some investigations of this phenomenon, and the results of his work were incorporated in his thesis for graduation, and the data were published in the proceedings of the Agricultural College of Indiana, Purdue University, for the year 1882.

In 1886 Jensch noticed that when lime and tricalcium phosphate were ignited together and the resulting mass pulverized, both citric acid and neutral ammonium citrate would extract phosphoric acid from the powder.<sup>1</sup>

In 1887, I published in *Agricultural Science* (March number) an article on the use of phosphorus contained in iron ores as a fertilizing material, after the conversion of the ores into iron or steel.

In 1889, I received from the Pottstown Steel Works a sample of phosphatic slag which was sent me under the name of cinder.

The superior merits of basic phosphatic slags as a fertilizer led me to believe that they might be largely soluble in neutral citrate solution. I therefore had this sample examined by Messrs. McElroy and Krug with that object in view. It was found to contain 20.20 per cent. total phosphoric acid, of which 12.25 per cent. were soluble in neutral ammonium citrate, the official solution used for the analysis of phosphatic fertilizers. An account of this property was published in the *Journal of Analytical Chemistry*, October, 1889. In this paper it is stated: "From the above results it is seen that in the phosphate slag we have a form of phosphoric acid equivalent in value to a first-class superphosphate."

<sup>1</sup> *Ber. d. chem. Ges.*, 19, 3093.



Petermann, in 1889, called attention to the fact that the calcium phosphatic limestone gives up phosphoric acid to a citrate solution.<sup>1</sup> In 1890 Jensch proposed the use of citric acid for the separation of tetra- from tri-calcium phosphate.<sup>2</sup> In 1892 Foerster published the statement that tetracalcium phosphate is easily soluble in ammonium citrate solution.<sup>3</sup>

Wagner proposed a special ammonium citrate solution having an excess of citric acid as a solvent for the tetracalcium phosphate in basic slags, and published an account of it in 1893.<sup>4</sup>

Since then the literature on this subject is very extensive, and it would be out of place here to attempt to cite the papers which have been published. It appears, from a study of the literature, that the first published account of the application of ammonium citrate as a method of valuing the availability of phosphatic slag was made from this laboratory in the paper published in the *Journal of Analytical Chemistry* above noted. For some reason, however, the method itself is universally known as the Wagner process.

Experience has shown that the official method of determining available phosphoric acid, applicable to the reverted phosphoric acid in superphosphates, is of varying value when applied to phosphatic slags. The composition of phosphatic slags has been previously described by Krug and myself.<sup>5</sup> It is evident that the tetrabasic lime phosphate is less stable than the tricalcium phosphate and hence the phosphoric acid which it contains is more readily given up to the growing plant. When a basic phosphatic slag is treated with neutral ammonium citrate in the regular official manner, the quantity of phosphoric acid which passes into solution is, as a rule, far less than the available content of phosphoric acid as indicated by the effect of the fertilizer upon a growing crop. For this reason other methods of determining available phosphoric acid have been proposed and the one now in use is known as the Wagner process in which a strongly acid ammonium citrate solution is used as a solvent.<sup>6</sup> The method of solution employed is a purely arbitrary one but gives results generally comparable to the effects produced in the field.

<sup>1</sup> *Chem. Centrbl.*, 1889, 2, 1036.

<sup>2</sup> *Ztschr. angew. Chem.*, 1890, p. 504.

<sup>3</sup> *Ztschr. angew. Chem.*, 1892, No. 113.

<sup>4</sup> *Chem. Ztg.*, 13, 1153.

<sup>5</sup> *J. Anal. Appl. Chem.*, 5, p. 685.

<sup>6</sup> *Wiley's Agricultural Analysis*, 2, 80.



No. 1. X 60.

Greater than 0.25 millimeter in diameter.

No. 2. X 60.

From 0.10 to 0.25 millimeter in diameter.

No. 4 X 60.

No. 3 X 60.

No. 1 X 60.

The action of this solvent on phosphatic slags is very different for different samples. In some cases almost the whole of the sample is composed of pure tetracalcium phosphate and in these instances the solvent action of the reagent is very high. In other cases the sample may contain tricalcium phosphate, particles of silicious slags and also of iron and steel. In these instances, a low solvent action is noticed. It therefore has seemed desirable to supplement the chemical analysis of the slags with a mechanical separation. For particles of one-tenth of a millimeter in diameter and above, this separation is easily effected in a series of sieves, the finer sieves being made of bolting cloth. It is evident that a further separation of the fine particles cannot be secured with water, by reason of the action of this reagent upon the free lime which the slag contains.

About four years ago, I made some experiments looking to the substitution of alcohol in the place of water in the mechanical analysis of soils. The preliminary experiments succeeded so well that it was deemed advisable to use alcohol for securing the separation of the finer particles of the slag. The separations were made for me by Mr. C. C. Moore of the laboratory staff. The method of procedure is as follows: From twenty to fifty grams of the slag are placed in a shaking bottle and vigorously agitated for a few minutes on a milk-shake machine with ninety per cent. alcohol. This treatment serves to break up all the flocculates the sample may contain. The sample is placed in beakers entirely similar to those which are used in the mechanical separation of the soils by the subsidence method.

At first it was only desired to secure two series of separates of the fine particles and these were obtained by an arbitrary time of subsidence. All the particles which remained in suspension in a column of fifteen cm. of alcohol for five minutes were collected together and marked as separate No. 5. When all the particles which thus remained in suspension had been removed, another separation was made consisting of those particles remaining in suspension in like conditions, for two minutes and a half. This portion of the sample was collected and was designated as separate No. 4. The remaining portion of the sample was freed of alcohol and separated into three portions by sifting through two sieves made of bolting cloth with meshes of one-tenth and one-quarter of a millimeter diameter respect-

ively. All that portion passing through the one-tenth millimeter mesh is designated as separate No. 3. The portion passing the quarter millimeter mesh but not passing the tenth millimeter mesh is designated as separate No. 2. The portion not passing through the quarter millimeter mesh is designated as separate No. 1. The remarkably uniform size of these separates is shown by the accompanying photographs in which they are represented as magnified sixty diameters. By an inspection of separate No. 5, it is seen that it could be easily divided and another finer portion be secured, by means of a ten minutes subsidence in alcohol.

The alcohol used for the separation is of ninety per cent. strength.

The original sample and the separates were subjected to a chemical analysis, conducted for me by Mr. E. G. Runyan of the laboratory staff. The analytical work was confined to a determination of the total phosphoric acid and that soluble in the Wagner reagent. The data obtained follow :

	Original sample.	Separate No. 1.	Separate No. 2.	Separate No. 3.	Separate No. 4.	Separate No. 5.
	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
Total $P_2O_5$ .....	16.54	13.91	16.14	16.71	18.21	18.16
Citrate soluble $P_2O_5$ ...	11.67	6.24	10.85	12.21	13.65	14.91
Proportion of original sample		12.00	33.00	26.00	8.00	21.00

From the above analyses, it is seen that the separates four and five contain not only the highest total quantity of phosphoric acid, but also the highest available acid. It is seen that there is a regular progression in the richness and availability of the sample from the coarsest to the finest parts. The relative proportions of the different separates to the whole are shown in the table. The data lead to the inference that it may be advantageous to the manufacturer of basic slags to secure at least a partial separation, in some such manner as indicated, for the purpose of being able to place on the market a more concentrated and available fertilizing material. The annual product of basic phosphate slags now amounts to about 1,500,000 tons and the output is rapidly increasing. Up to the present time American analysts have not had occasion to examine many samples of phosphatic slags but it is certain, in the near future, that the consumption of this material in the United States will rapidly increase. It is important, therefore, that investigations be made looking to the best methods of chemical and mechanical analysis.

## PREPARATION OF SODIUM NITROPRUSSIDE.

BY F. S. HYDE.

Received November 18, 1896.

**T**HE literature referring to this compound is usually more or less incomplete in regard to the details of its preparation; but, unless it is prepared in the pure state, its use as a delicate reagent is somewhat impaired.

Place sixty grams pulverized potassium ferrocyanide in a medium-sized evaporating dish, and pour on it a solution consisting of 150 grams concentrated nitric acid (sp. gr. 1.42) diluted with 100 cc. of water. Perform the operation under a hood or in a draft of air. When the evolution of gases has ceased, evaporate on a water-bath with occasional stirring until a few drops of the liquid, mixed with water in a test-tube, no longer give a blue color with ferrous sulphate solution but, instead, a dark greenish cloud.

It may be necessary to continue the evaporation for an hour or more before the final test is obtained. However, the liquid which has a dark reddish brown color, should be evaporated to about one-half of its original bulk to insure success. Allow to cool slowly over night, when crystals of potassium nitrate, blackened with impurities separate out in stellated masses or needles.

Decant the liquid from the crystals (which are rejected) and neutralize it by stirring in dry sodium carbonate, producing a greenish brown froth and a red solution. This will require some patience on account of frothing; heat on the water-bath, filter and wash. Evaporate the red filtrate to one-half of its bulk or more, and allow it to crystallize by slow cooling on the water-bath.

The crystallization consists mostly of crusts of sodium and potassium nitrates, together with little red needles of nitroprusside. Pour off the mother liquor and treat the impure crystals with as little water as possible just enough to dissolve the nitrates and leave the red crystals. Then with this nitrate solution in the same dish, wash or "pan out" (with a rotary motion) the impurities from the crystals.

These red crystals may be recrystallized by dissolving in a small quantity of distilled water and evaporating the deep-red

solution in a beaker to small bulk, or better still until there is an incipient formation of crystals.

By slow cooling, as before, clusters of beautiful red rhombic needles are produced. Pour off the mother liquor and dry the crystals on filter paper.

The yield averages about twenty-five per cent. by weight of the ferrocyanide used. In one experiment, the writer obtained seventeen grams of the nitroprusside from sixty grams ferrocyanide, or over twenty-eight per cent. yield. Very little is gained by treating the mother liquors for an extra yield, especially in the case of small amounts.

Sodium nitroprusside ( $\text{Na}_2\text{Fe}(\text{NO})\text{Cy}_2 + 2\text{H}_2\text{O}$ ) has no melting point. When heated in a glass tube, the crystal gives off moisture and becomes black without disintegration. It is slowly soluble in cold water, but easily soluble in hot water. It is best known as a very delicate reagent for sulphur in the form of alkaline sulphides, producing violet colored solutions which gradually lose color on standing.

Certain organic compounds also react with sodium nitroprusside. For instance, with a weak aqueous solution of nitroprusside made slightly alkaline with caustic soda, formaldehyde gradually produces a dark amber tint; acetic aldehyde gives a blood-red color, becoming darker on standing, and finally violet after two or three hours; acetone produces a blood-red solution fading gradually to orange-red; and benzaldehyde gives no coloration.

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## IMPROVEMENTS IN THE COLORIMETRIC TEST FOR COPPER.

BY GEORGE L. HEATH.

Received November 9, 1896.

THE modifications of Heine's "blue test" described in some of the text-books<sup>1</sup> recently issued, admit of some improvement in speed of operation, ease of manipulation (in presence of the large amounts of iron, alumina and silica in poor slags or tailings), and finally in the making of the standard colors from solution of pure copper.

Having made a study of the process, and having had it in use

<sup>1</sup> Furman's Manual of Practical Assaying, 1895, p. 159; Kerl's Metallurgy of Copper; Peter's Modern Copper Smelting, 1895, p. 65.

several years at a large smelting works, modifications have been adopted which certainly present a few advantages, and a full description may be of interest to those who have occasion to use the test in technical work.

It is one of those tests where the principle is a very simple one, *i. e.*, the matching of colors of ammoniacal solutions of pure copper, but in which any improvement must be made in the small, but important, details of operation.

Copper has usually to be determined in tailings or lean blast furnace slags, and must be separated from silica, and oxides of iron, alumina, and lime.

The best conditions for effecting a complete separation have been made the subject of experiments detailed in this paper. The first authority quoted directs that "a standard of pure copper should be run with each set of assays, as the color fades on standing." That is true of standards made according to Furman's Manual, but it is possible to make color standards of ammoniacal solution of pure copper, which are very permanent, having been kept for a year without alteration. Stability of color may be secured if the following facts concerning the behavior of ammoniacal copper solutions be understood and applied.

It is easily proved that if ammonia be added to a very dilute solution of nitrate, or better, the sulphate of copper, until the basic salt redissolves in excess of alkali, the color produced is first purple, then purplish-blue, and finally with a large excess of ammonia, a clear and more permanent blue.

The blue color may then incline to greenish, if there is any organic matter in the reagents or substance analyzed, for a trace of organic matter in solution is apt to prevent the complete precipitation of ferric oxide by ammonia, and the trace yet dissolved, produces a greenish tint in the ammoniacal copper solution.

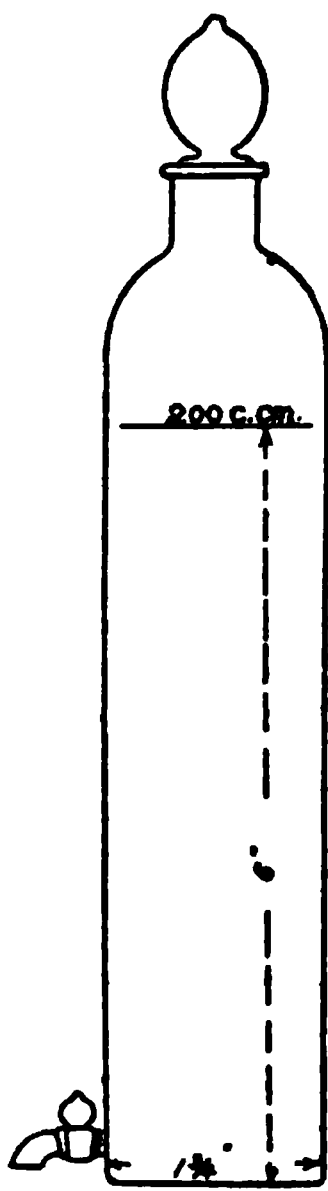
The color of standards for "blue tests" is found to be very permanent, (1) if the nitric acid used to dissolve the copper be replaced by sulphuric, (2) if the excess of ammonia be sufficient to produce the clear, neutral blue, and (3) if the color standards be kept in colorless glass bottles with very tightly fitting glass stoppers, preventing the slightest evaporation or loss of ammonia.

## DIRECTIONS FOR PERMANENT STANDARDS.

Weigh a little over three-tenths gram of pure copper, place it in a flask or tall, narrow beaker, and dissolve it in five cc. of C. P. nitric acid (sp. gr. 1.40) and five cc. of sulphuric acid (sp. gr. 1.84). Evaporate carefully until the latter begins to evolve white fumes, and then cool, add twenty-five cc. of distilled water, and strong ammonia in sufficient excess to produce a clear solution again.

Prepare at least three liters of dilute ammonia (one volume to six parts by volume of distilled water) and dilute the copper with this until one cc. of the liquid contains exactly 0.0025 gram of pure copper, since two and a half grams of substance are always taken as a basis, and the degree of dilution then permits the whole range of colors to be made and diluted to a standard volume of 200 cc.

Measure accurately the portions of standard solution required for a set of colors, from 0.10 to 1.30 per cent. copper and make each one up to 200 cc. with the dilute ammonia. By this means a uniform tint and gradation of color is secured throughout the series.



The standards are kept in tall cylindrical bottles of thin, colorless glass, provided with accurately ground glass stoppers and having a mark on the side at 200 cc. They must be of strictly uniform thickness and diameter; the dimensions for a convenient size are shown in the sketch. (Extra bottles for the analyses might be provided with a stop-cock, as in a Hehner's colorimeter.) Screw the stoppers in very tightly, mix by shaking, and keep in a rather cool place, protected from direct sunlight.

With the exception of one bottle, whose stopper had become loose a few days ago, a set of such standards bottled January 1, 1896, do not differ from freshly prepared solutions of pure copper. (Refer to Experiments 1 and 2). The color of the one mentioned was remedied by filling to the mark with a few drops of strong ammonia.



ANALYSIS OF LEAN CUPRIFEROUS MATERIAL.

Crush and reduce the sample until the final portion, sufficient for analysis, will pass a one-hundred mesh sieve. If any pellets remain on the sieve, they should be weighed and determined separately.

It is considered better to take for analysis two and a half grams (or of material over one and two-tenths per cent., 1.25 grams) rather than one-half gram, as prescribed by some writers, since the decomposition is fully as rapid, and an occasional fine particle of metal, or difference in sampling, will introduce less error in the calculated percentage. If, however, only one-half gram should be taken, this test could be used with material containing nearly six per cent. copper. The method finds its best application between zero and two per cent.

Place the weighed sample in a No. 4 porcelain casserole four and a quarter inches in diameter at the top; barely moisten it with water to prevent caking, then add fifteen cc. of nitric acid (sp. gr. 1.42), and warm gently over a wire gauze until the covered dish is filled with red fumes, but not long enough to evaporate the acid. Remove, stir the mass, and break up any clots which may adhere to the dish.

When the decomposition appears to be complete, or all the copper dissolved, add five cc. of sulphuric acid (sp. gr. 1.84), place the covered casserole on a wire gauze or plate, and boil until the nitric acid is nearly driven off, and the mass has become a thick, but rather soft, paste. This insures the dehydration of the silica, and the change of copper to sulphate. From this point onward three practical modes of procedure are recognized, the choice of which depends on the judgment of the analyst, who may perform the following tests :

1. A working test, approximate, involving one precipitation of iron and alumina by ammonia and separation of the copper by filtration, and washing.

2. An accurate test, involving the previous separation of copper from the acid solution by reduction with aluminum. (See text-books.)

3. By the author's plan of a double precipitation by ammonia, which is sufficiently accurate and much more rapid than the second alternative plan, as will be evident from a later description.

I. To complete the working test, cool the residue in the casserole somewhat, add 120 cc. of water, washing the glass cover, stir well, heat until quite warm to the hand, and then add quickly enough ammonia (sp. gr. 0.9) to precipitate iron and alumina, and cause the liquid to smell very strongly.

Filter, with the aid of a pump, through a fifteen cm. German filter into one of the glass bottles, and wash the precipitate by repeated additions of dilute ammonia (1 : 10) until the bottle is filled to the mark, allowing each portion to run through before the next is added. When the mark is reached, allow ten cc. of washings to run into a tube placed against a white paper, and if no color is detected the washing is finished.

A thorough stirring of the precipitate with a rod after each addition of wash water is essential to the most complete extraction of copper. If the slag or tailings contain less than one per cent. of copper, the extraction is sufficiently complete for approximate working tests. (Refer to the appended table of experiments.)

In the presence of a large percentage, twenty-five per cent. or more, of oxides of iron and aluminum, the copper retained in the precipitate may be considerable, if the working is faulty, but will not generally run over 0.05 per cent. This error is, in the long run, pretty nearly balanced by the tendency to read the colors too high if the shade reaches to greenish-blue instead of blue. A purplish tint in the filtrate indicates, however, that sufficient ammonia was not added to effect the most complete separation of copper.

If this purplish tint in the blue is very pronounced an assay should be repeated, but if slight it may be remedied by the addition of ammonia, for which allowance is made by calculation in taking the color reading.

II. Accurate Method. The copper may be separated from the major part of the basic oxides by adding thirty cc. of water and five cc. of sulphuric acid to the decomposed slag in casserole, then adding a piece of aluminum (one inch square and one-sixteenth of an inch thick), and boiling gently till the copper is reduced.

Remove the aluminum to a beaker, filter the solution, and wash once. Then dissolve any particles of copper from the aluminum with hot dilute nitric acid (one part acid to two of water),

transfer as much as possible of the precipitate to the casserole, and pour the acid solution from the beaker through the filter, allowing the liquid to run into the casserole. After the copper is dissolved from the filter add three cc. of sulphuric acid, cover the casserole, and boil down with a moderate heat to remove nitric acid.

Finally, precipitate by ammonia, filter, and wash as usual. This, however, offers more chances for error, and is certainly less simple and rapid than the third alternative method proposed (that of double precipitation), as follows:

III. To the contents of the casserole, after boiling the material with nitric and sulphuric acids, add only seventy cc. of water, stir well to dissolve copper sulphate, then add rapidly an excess of ammonia (thirty cc. is generally sufficient), filter on a fifteen cm. filter, and wash twice with ten cc. of dilute ammonia (one part ammonia to ten of water). By means of a rod, and fifty cc. of water measured into a small wash bottle, transfer the precipitate as completely as possible to the casserole without damaging the paper. Add, drop by drop, enough sulphuric acid to just redissolve the iron or alumina, then follow with twenty to twenty-five cc. of ammonia (sp. gr. 0.9), or sufficient to precipitate the oxides again and cause the liquid to smell strongly. Filter and wash with dilute ammonia as usual. After stoppering and shaking the bottles the colors may be read within 0.03 per cent. by placing the bottle close to one of the standards against a window pane and placing a piece of perfectly white, unruled paper behind them.<sup>1</sup> Three bottles should never be placed closely together, as the middle one will appear too light.

A table of experiments is appended which shows the effects of variations in the working conditions. The battery assays are those of the same solutions whose color readings are given in the adjoining column, and since there are no impurities in the products tested to interfere with a battery assay, electrolysis furnishes an accurate estimation of the true amount of copper in solution and in the iron and aluminum precipitates which were dissolved in dilute sulphuric acid and electrolyzed. Most of the filtration, etc., was made by an assistant. A = Chemist, B = Assistant Chemist.

<sup>1</sup> Copper assaying on Lake Superior: *Eng. and Min. J.*, April 20, 1895, p. 369.



In the experiments with the approximate working test, the colors were read without any attempt to dilute to an exact match with the next lower standard, but the difference between the assay and the next lower and higher bottles was estimated by the eye, which, with practice, can be done within 0.03 per cent.

The tests marked "purplish" were not read until the shade (or tint) was corrected to that of the standards by the addition of a few cc. of ammonia.

If the first residue be boiled too dry, or the color be very purple after filtration, it will generally prove that the separation of copper from basic oxides by one precipitation with ammonia is very incomplete.

If the color be greenish there is a general tendency to read the colors a little too high, but the difference is generally slight and entirely within the limits of error in sampling. If the greenish tint be very pronounced the assay should be repeated, and if the trouble be due to the cupriferous material, the portion weighed for analysis should be kept for several minutes in a porcelain crucible at a full red heat and stirred with a platinum wire.

The writer recommends the general methods here given, in preference to those already in print, for reasons which have been specified, and considers modification No. 3 a better technical method than any one involving reduction of copper by aluminum for the following reasons:

*a.* A second precipitation of oxides of iron and aluminum will remove all but a trace of copper, if the washing be carefully completed, even when the material is rich in basic oxides.

*b.* No extra time is required for the second precipitation, since this dispenses with part of the necessary washing.

*c.* There is always a possible danger of incomplete reduction of copper by aluminum or of retention by the silica of a little copper (which would be extracted by ammonia), and more time is required, especially if the silica be removed by filtration before reduction with aluminum.

# ON THE DETERMINATION OF STEARIC ACID IN FATS.

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**T**HE quantitative determination of the individuals composing the mixture of fatty acids obtainable from any fat or oil is one of the most difficult problems of analytical chemistry and one which is very far from solved at the present time. Apart from the determination of certain constants, such as the iodine absorption, amount of potassium hydroxide consumed, etc., little more can be done than a rough separation of saturated from unsaturated fatty acids. A quantitative separation of the unsaturated fatty acids has barely been attempted, if we except the determination of the amount of hexabromide obtainable from the mixed fatty acids of linseed and other drying oils, measuring the linoleic acid, to which one of us referred at a recent meeting of the Society of Public Analysts, and concerning which we hope to publish the results of our joint work at an early date. The few figures published by Hazura, based upon the proportions of hydroxy acids obtained by the action of potassium permanganate upon unsaturated fatty acids, are obviously very rough and of no practical value.

For the separation of the solid fatty acids no quantitative method of any kind exists and here again inferences based upon the determination of physical constants and of the equivalents of mixtures have been the only available means. If it be known that a mixture contains two saturated fatty acids only and no more, the determination of the melting point or of the molecular equivalent is a satisfactory way of arriving at their relative proportions. But unfortunately there is no practicable method of proving that two and only two acids are present and, hence, all determinations hitherto made must be accepted with a considerable amount of doubt.

Heintz's well-known method supplies the only means of obtaining an insight into the qualitative composition of a mixture of non-volatile fatty acids, and Liebig's analogous method a means of examining a mixture of volatile fatty acids. Heintz's method is, however, solely a qualitative one and appears unsuited for analytical purposes. Without frequent repetition of the fractional precipitation nothing like a perfect separation of two closely allied fatty acids can be obtained. As, however, we

could find but few data on this point in the literature, we thought it advisable to ascertain to what extent Heintz's method was capable of concentrating the fatty acid of higher molecular weight from a mixture of known composition, by a single precipitation only.

#### FRACTIONAL PRECIPITATION.

*Stearic Acid.*—A considerable quantity of fatty acids obtained in the usual manner from cocoa-butter was dissolved in as little hot alcohol as possible, and when cold, the crystallized mass was pressed in a linen cloth. The residue was again dissolved in hot alcohol and the residue again pressed. After repeating this crystallization ten times the melting-point remained constant at  $68.5^{\circ}$  C. (Heintz gives  $69^{\circ}$  C. as the melting-point of stearic acid), and had a molecular weight of 283, as determined by the amount of potassium hydroxide consumed and the percentage of barium in the barium salt. (Theory for stearic acid, 284.)

*Palmitic Acid.*—In most of our experiments we made use of pure palmitic acid obtained from palm oil and prepared by Hopkin and Williams. This melted at  $61.8^{\circ}$  C. (Heintz,  $62^{\circ}$  C.), and had a molecular weight of 255.5 (theory 256). Subsequently we prepared palmitic acid from Japan wax. To the experiments made with the latter we shall refer later on.

*Precipitation with Barium Acetate.*—A solution of barium acetate was prepared containing 8.94 grams of barium acetate in 100 cc. of water, of which solution five cc. contained 0.241 gram barium, capable of combining with one gram of stearic acid. The mixed fatty acids were dissolved in 100 cc. of hot (methylated) alcohol of ninety-eight per cent., and the required quantity of barium acetate solution was added drop by drop from a burette to the hot alcoholic fatty acid solution, which was shaken after the addition of every drop. After cooling the precipitates were filtered off, thoroughly washed with cold alcohol of ninety-eight per cent., dried in the water-bath, and the barium contained in them determined by ignition with sulphuric acid. From the amount of barium sulphate obtained the molecular equivalent of the precipitated fatty acids was calculated and from this the amount of stearic acid by the formula :

$x = \frac{284(m-256)}{m(284-256)}$  where  $x$  is the required amount of stearic acid,  $m$  the molecular equivalent found, and 284 and 256 the equivalents of stearic and palmitic acids, respectively.

The filtrate and washings from the first precipitate were mixed and a second fraction of the fatty acids remaining in solution precipitated with barium acetate solution and treated as before. In some cases a third and fourth precipitation was made. The results are given in the following table :

I.							
Stearic acid. Grams.	Palmitic acid. Grams.	Barium acetate solution added. cc.	Barium salt. Grams.	Containing barium.	Molecular weight of fatty acids.	Stearic acid in precipitate. Per cent.	Weight of re-covered stearic acid.
1	1	5	(1) 0.9614	0.1919	275.5	71.7	0.549
		5	(2) 0.4326	0.09	261.75	22.2	0.076
		5	(3) Too small for accurate estimation.				0.625
1	2	5	(1) 1.0046	0.2021	272.9	62.8	0.5039
		5	(2) 0.9696	0.1985	273	63	0.4983
		5	(3) 0.5122	0.1066	261.6	22.3	0.0904
							1.0926
1	3	5	(1) 0.8830	0.1827	263.2	27.9	0.1953
		5	(2) 0.9100	0.1863	267.3	42.8	0.3097
							0.5050
1	3	5	(1) 0.8920	0.1842	264.4	30.9	0.2187
		5	(2) 1.0315	0.2125	265.2	35	0.2866
							0.5035
0.5	0.5	2.5	(1) 0.5376	0.1082	272.8	62.7	0.2692
1	1	2.5	(1) 0.5246	0.107	268.3	46.6	0.1946
		2.5	(2) 0.5262	0.1065	270.4	54	0.2266
							0.4212

As a further means of getting some idea of the composition of the precipitated fractions, we recovered the fatty acids by shaking the barium salts with ether and hydrochloric acid in a separating funnel, washing the ethereal solution several times with water, evaporating the ether, and determining the melting-point of the mixed fatty acids. We thought it well to check,



on this occasion, the table of melting-points constructed by Heintz, referring to mixtures of stearic and palmitic acids. The following are our results, in comparison with Heintz's.

## II.

Stearic acid. Per cent.	Palmitic acid. Per cent.	Heintz <sup>1</sup> M. P. ° C.	Hehner and Mitchell. ° C.
100	0	69.2	68.5
90	10	67.2	66.5
80	20	65.3	64.2
70	30	62.9	61.5
60	40	60.3	59.4
50	50	56.6	55.6
40	60	56.3	55.5
32.5	67.5	55.2	54.5
30	70	55.1	54.2
20	80	57.5	56.5
10	90	60.1	59.0
0	100	62.0	61.8

It will at once be seen, by a glance at these tables, that any judgment as to the composition of a mixture of stearic and palmitic acids based on the melting-point can only be very roughly approximate, especially when the acids are present in about equal proportions, there being only about 1.5° C. difference between mixtures containing fifty and thirty per cent. of stearic acid. Still, it enabled us to some extent, to confirm the results given in the first table, obtained by determining the equivalents of the mixed acids. In the following table results are given based on the melting-points only :

## III.

Stearic acid.	Palmitic acid.	Barium acetate solution added. cc.	Melting-point. ° C.	Approximate percentage of stearic acid in precipitate.
0.5	0.5	(1) 2.5	60.8	60-70
		(2) 2.5	54.6	about 30
1	1	(1) 2.5	59.4	60
		(2) 2.5	59.0	nearly 60
		(3) 2.5	58.6	50-60
		(4) 2.5	54.2	30
0.5	1	(1) 2.5	57.0	about 55
		(2) 2.5	55.8	" 50
		(3) 2.5	54.2	30
2.1	0.9	(1) 2.5	64.0	nearly 80
		(2) 2.5	65.0	80-90
		(3) 2.5	65.8	80-90
		(4) 2.5	60.5	60-70
		(5) 2.5	54.6	30-40

<sup>1</sup> *Ann. Chem. Pharm.*, 92, 295.

It is obvious from these results, that by means of an aqueous solution of barium acetate, used in the proportions stated, but a very moderate concentration of the higher fatty acid can be accomplished in one precipitation. Curiously enough, it not infrequently happens, that the second fraction contains a larger percentage of the higher fatty acid, than the first portion. Quantitative results cannot possibly be obtained.

*Precipitation with Lead Acetate.*—As it might be thought, that owing to the employment of an aqueous solution and the consequent somewhat sudden separation of the precipitate a less perfect fractionation took place than if the precipitate were allowed to form very slowly, we repeated the fractionation with the employment of an alcoholic solution of lead acetate. A solution, containing 6.67 grams of the salt in 100 cc. of alcohol, of which ten cc. were capable of completely precipitating one gram of stearic acid, was made, and the required amount of this solution was added slowly to the hot alcoholic solution of the mixed fatty acids. The fraction crystallizing out on cooling was treated as described in reference to the preceding table.

## IV.

Stearic acid. Grams.	Palmitic acid. Grams.	Lead acetate solution added. cc.	Melting-point of liberated acids.	Approximate per- centage of stearic acid. Per cent.
0.5	1	(1) 5	60.2	60-70
		(2) 5	55.0	30-40
		(3) 5	55.4	30-40

Here again the separation was no more complete than in Tables I and III.

*Precipitation with Magnesium Acetate.*—A solution containing 18.835 grams of magnesium acetate in 500 cc. of which ten cc. were required to precipitate one gram of stearic acid was made and used in the following experiment:

## V.

Stearic acid. Grams.	Palmitic acid. Grams.	Magnesium ace- tate solution added. cc.	Melting- point.	Approximate percentage of stearic acid.
0.5	0.5	5	62	About 70

By these results we were confirmed in our opinion, that while by oft repeated fractionation a mixture of fatty acids may be

made to yield the highest fatty acid in a comparatively pure condition, by a single precipitation no sharp separation can even approximately be obtained however slowly the separation be allowed to take place. When more than two fatty acids are present in a mixture, the results must be still more doubtful. For quantitative analytical work, for which, of course, the method was never intended, it is not applicable.

After numerous attempts to separate the liquid and the solid fatty acid from each other by means of glacial acetic acid, which readily dissolves oleic, but at the same time not inconsiderable amounts of palmitic and of stearic acids, and by mixtures of acetic acid, alcohol and water (after the method of David<sup>1</sup>), we came to the conclusion that nothing like a sharp separation could thus be effected. Somewhat better were the results obtained by the use of dilute alcohol alone. On grinding up fatty acid, as obtained by the saponification of a solid fat and decomposition of the soap, with dilute alcohol (sp. gr. 0.911) in a mortar, we found that the unsaturated fatty acids were completely dissolved, the palmitic acid partially so, while the stearic acid remained almost completely undissolved. From ten to twenty grams of the various fatty acid mixtures were thus ground up with 100 cc. of dilute alcohol, the latter removed by a filter-pump and the residue was washed with 100 cc. of dilute alcohol of the same strength. After pressing the residue in a filter-cloth, placed between blotting paper, a pearly white mass was obtained, which after drying, showed an iodine absorption of from two to three per cent. From the molecular weight, ascertained by means of alcoholic alkali, the proportions of palmitic and stearic acids were calculated on the assumption that nothing but stearic and palmitic acids were present, an assumption which cannot be very incorrect, because the lower fatty acids are soluble to a considerable extent in alcohol of the strength mentioned.

<sup>1</sup> *Compt rend.*, 86, 1416.

## VI.

	Fatty acids. Grams.	Washed resi- due. Grams.	Molecu- lar weight.	Per cent. stearic acid in the washed acids.	Per cent. stearic acid in original acid.	Iodine number of original fatty acid.	Melting-point of original fat- ty acids.
Butter (Brittany)....	10	2.0	260.8	15.0	3.0	....	....
Same sample.....	..	..	259.3	....	....	....	....
	..	..	260.3	....	....	....	....
Butter (Danish) ....	20	2.5	263.6	29.0	3.6	....	....
	..	..	263.8	....	....	....	....
Butter (Danish) ....	10	1.85	258.0	7.0	1.29	....	....
Oleomargarine.....	10	4.0	267.3	428.	17.12	46.5	43.2
Margarine .....	10	3.7	266.2	40.0	14.8	43.23	38.0
Margarine .....	10	4.0	265.0	34.4	13.76	....	....
Mutton tallow .....	10	5.5	264.0	30.0	16.5	39.5	43.8
Mutton tallow .....	20	11.0	265.8	37.4	19.47	35.6	47.8
Lard.....	20	7.5	258.8	8.6	3.2	....	....
Lard.....	20	7.0	260.0	15.0	5.2	....	....

Although, when working under exactly the same conditions, fairly constant results could be obtained, the method effected at best only a concentration of the stearic acid and afforded no certainty that the final product consisted of only two fatty acids, from the equivalent of which the proportion might be calculated. Although we worked as nearly as possible at a uniform temperature, variations could not be avoided, leading us to abandon the search in this direction.

The following reasoning gave much greater hopes of success. Imagine a mixture of fatty acids to be treated with an amount of solvent sufficient to dissolve the whole of the various components of the mixture. If the solvent were already saturated with one of the constituents of the fatty acid mixture to be examined, it was to be expected that the totality of the corresponding fatty acid contained in the mixture would remain undissolved. Or, if a mixture were heated with a solvent saturated at a certain temperature with one of the constituents sought to be determined, then on cooling down to a corresponding temperature, the whole of the particular constituent might be expected quantitatively to crystallize out, provided that the other constituents of the fatty acid mixture exercised no restraining influence by adding to the solubility.

In principle this is the method of Casamajor for the quantitative separation of cane sugar from invert sugar. Casamajor washed the sugar to be examined with methyl alcohol saturated with cane sugar.

We chose the freezing-point of water as the most suitable constant temperature, it being easily maintained and the solubility of stearic and the other acids occurring in fats being suitable for accurate work.

After some preliminary experiments with ether and other solvents which we had to reject as taking up too much stearic acid, we finally fixed upon alcohol (methylated) of a specific gravity of 0.8183, containing 94.4 per cent. of alcohol by volume. It will be seen, in the following experiments, that the exact strength of alcohol is a matter of no consequence, but the solubility determinations here to be given apply only to alcohol of that strength.

For maintaining a constant temperature we employed an ice-chest, constructed of a metal box, to the interior side of which were soldered suitable sockets to receive the clamps necessary to hold the small flasks in which the determinations were carried out, submerged up to the neck in ice-water. The metal box was fitted in a wooden box and the space between metal and wood was packed with wool and saw-dust, while a cushion of wool and flannel was placed between the lids of the metal and wooden boxes.

For the preparation of the stearic solution about three grams of pure stearic acid were dissolved in about a liter of warm alcohol of 0.8183 sp. gr., and the stoppered bottle containing the solution was placed over night in the ice-water (in which were lumps of ice) in the chest, so that the bottle was submerged up to the neck. After twelve hours a considerable portion of the stearic acid had crystallized out. The saturated mother liquor was siphoned off without removing the bottle from the ice-water. The filtering siphon used consisted of a small thistle funnel twice bent at right angles, fitting with its smooth limb in a flask attached to a suction pump, while the bulb of the funnel, which was submerged in the ice-cold solution, was covered over with a piece of fine calico. On applying suction a perfectly clear stearic

solution was obtained, saturated at  $0^{\circ}\text{C}.$ , or rather at  $0.2^{\circ}\text{C}.$ , which was the temperature almost constantly shown by a standard thermometer.

A precisely similar mode of filtration was also adopted in the quantitative experiments on mixed fatty acids, the thistle-funnel used being a miniature one, with a bulb not larger than about one-quarter of an inch in diameter. The accompanying drawing will sufficiently explain the apparatus.

## VII.

SOLUBILITY OF STEARIC ACID IN ALCOHOL (SPECIFIC GRAVITY 0.8183),  
AT  $0^{\circ}\text{C}.$

Stearic acid taken. Gram.	Alcohol. cc.	Time of cooling. Hours.	Residue obtained by evaporating ten cc. of the filtered solution. Gram.
0.2	100	12	0.0155
0.2	100	36	0.0153
0.2	100	84	0.0153
0.5	100	12	0.0158
0.5	100	36	0.0145
0.5	100	84	0.0140
0.3	100	48	0.0144
0.3	100	84	0.0142
0.3	100	12	0.0157
0.3	100	36	0.0149
0.4	100	12	0.0158
0.4	100	36	0.0148

## VIII.

SOLUBILITY OF PALMITIC ACID IN ALCOHOL (SPECIFIC GRAVITY 0.8183)  
AT  $0^{\circ}\text{C}.$

Palmitic acid taken. Gram.	Alcohol. cc.	Time of cooling. Hours.	Residue obtained by evaporating ten cc. of filtered solution. Gram.
2	100	12	0.1298
2	100	36	0.1244
2	100	60	0.1211
2	100	84	0.1134
2	100	108	0.1086
2	100	132	0.1044
2	100	156	0.1028
2	100	12	0.1320

From the two preceding tables it appears that it is easy to obtain constant results with stearic acid, and that supersaturation does not readily occur. The solubility of the palmitic acid in alcohol of the same strength as that employed for stearic acid is about eight times greater than in the case of stearic acid, and constant results are far less easy to obtain.

*Experiments with Known Amounts of Pure Stearic Acid.*—Accurately weighed quantities of pure stearic acid were placed in weighed flasks capable of holding about 150 cc., provided with a rubber cork. From fifty to 100 cc. of the saturated stearic solution were added, the flask closed and the contents gently warmed on a water-bath till all stearic acid had dissolved. The flask was then clamped in the ice-chest and kept in ice-water over night. In the morning the contents of the flask were, as a rule, gently shaken, without being withdrawn from the ice-water, in order to promote crystallization and again left for at least half an hour. The alcohol was then filtered off by means of the arrangement described, care being taken to draw off the solution as completely as possible. The residue was washed three times successively with ten cc. of the saturated stearic solution, cooled down to 0° C. The small funnel was then detached from the suction arrangement and washed with hot pure alcohol, the washings falling into the flask containing the residue, the flask being previously taken out of the ice-chest. The alcohol was then evaporated, and the residue dried at 100° C. to constant weight.

Since the interior sides of the flask, as well as the residue of crystallized stearic acid, retained a small amount of the stearic alcohol, a small correction, experimentally found to amount to 0.005 gram had to be applied, this amount having to be deducted from the total weight found. In almost all cases the precipitated stearic acid formed a small, but compact mass after filtration, retaining a very minute amount only of the washing solution.

The following results were obtained.

## IX.

Stearic acid taken. Gram.	Saturated alcohol. cc.	Total residue found.	Stearic acid after de- ducting 0.005 gram. Gram.
0.0188	100	0.021	0.016
0.0220	100	0.025	0.020
0.0320	100	0.0381	0.0331
0.0381	50	0.0445	0.0392
0.1072	50	0.113	0.108
0.1356	100	0.1414	0.1364
0.1414	100	0.1440	0.1390
0.2137	100	0.2206	0.2156
0.2282	100	0.2334	0.2281

As a check we also made a number of experiments by dissolving weighed quantities of the stearic acid in the saturated alcohol, leaving the flask over night in ice and, instead of weighing the crystallized deposit, evaporated measured quantities of the filtrate, thus determining the amount of stearic acid in solution. If this corresponded with the amount previously found to be soluble in ten cc. of alcohol, it followed that the whole of the added stearic acid had separated.

## X.

Stearic acid. Gram.	Saturated alcohol. cc.	Residue in 10 cc. after twelve hours. Gram.
0.1955	100	0.0155
0.5090	100	0.0150
0.3130	100	0.0157
0.4010	100	0.0158

It will be seen that the amount left in solution perfectly corresponded with that contained in the stearic alcohol, and that therefore none of the added stearic acid could have remained in the solution.

Having thus satisfied ourselves, that pure stearic acid could be determined with a satisfactory degree of accuracy, it remained to be seen, whether in the presence of other fatty acids, equally satisfactory results could be obtained, or whether other fatty acids would themselves exercise a solvent action upon the stearic acid.



## XI.

## INFLUENCE OF LOWER SATURATED FATTY ACIDS.

Stearic acid taken. Gram.	Lower fatty acid employed. Gram.	Stearic acid found after deducting 0.005 gram. Gram.
0.0556	5 cc. butyric acid.	0.0582
0.0476	5 cc. acetic acid.	0.0468
0.0990	1.5 gram cocoanut fatty acids.	0.1070
0.1060	0.9079 cocoanut acids.	0.1118
0.2020	0.5130 " "	0.220

## XII.

## INFLUENCE OF PALMITIC ACID.

Stearic acid taken. Gram.	Palmitic acid added. Gram.	Stearic acid found, after deducting 0.005 grams. Gram.
0.2026	0.5472	0.2032
0.1016	0.5354	0.1074
0.0520	0.600	0.055

*Influence of Unsaturated Fatty Acids.*—The oleic acid used for the following experiment was commercial oleic acid, and was not free from stearic acid. Three grams crystallized in the manner described from stearic alcohol, giving 0.025 gram of stearic acid. A corresponding deduction had therefore to be made in the following experiment:

## XIII.

Stearic acid. Gram.	Crude oleic acid. Gram.	Stearic acid found. Gram.
0.2997	3.200	0.3355

Deducting from the latter figure 0.0278 gram, the amount of stearic acid obtainable from the three and two-tenths grams of oleic acid, and 0.005 gram for correction, there remain 0.3027 gram of stearic acid recovered from the 0.2997 taken, or one per cent. too much.

*Influence of Saturated and Unsaturated Fatty Acids Together.*—Fatty acids prepared from hog's lard were first crystallized by themselves and afterwards with different quantities of added stearic acid, with the following results:

## XIV.

Lard acids taken. Gram.	Stearic acid added. Gram.	Stearic acid obtained. Gram.	Added stearic acid recovered. Gram.
0.5	none	0.0242	.....
0.5	0.050	0.0738	0.0496
0.5	0.080	0.1058	0.0816

It is thus shown, that stearic acid added to a mixture of fatty acids can be completely recovered in the manner described.

*Experiments with Commercial Stearic Acid.*—The sample employed had an iodine absorption of two and three-tenths per cent. and melted at 56.2° C.

## XV.

Commercial acid taken. Gram.	Stearic alcohol added. cc.	Amount of deposit minus 0.005 gram. Gram.	Per cent. of stearic acid found.
0.1042	50	0.0490	47.02
0.1480	50	0.0702	48.7
0.2510	50	0.1223	48.7
0.2900	50	0.1468	50.6
0.3984	100	0.1932	48.5

## XVI.

## EXPERIMENTS WITH COMMERCIAL LARD.

Lard.	Iodine number.	Stearic acid minus 0.005 gram. Gram.	Stearic acid in fatty acids. Per cent.
1 0.9794	61.2	0.1338	13.06
2 0.5065	not taken	0.0635	12.53
2 0.8328		0.1090	13.08
2 1.0604		0.1359	12.90
3 0.4970	57.5	0.0801	16.11
3 1.0178		0.1634	16.05
4 1.0987	61.2	0.0669	6.09
4 0.9990		0.0764	7.6
4 1.2878		0.0782	6.07
5 0.5150	65.66	0.0548	10.64
5 1.0410		0.1030	9.89
6 0.5000	63.58	0.0372	7.4

*Determination of Stearic Acid in Fat from Different Parts of the Same Pig.*—It is well known that the proportion of liquid and solid fat varies very considerably in the fat taken from different parts of the same animal. We thought it would be of interest to ascertain whether in this case the alteration affected only the proportions of fluid (unsaturated) and solid fatty acids, or whether the latter themselves varied in composition. The animal from which the fat was taken was a Somersetshire pig six months old. The following table contains the results :

## XVII.

Part of pig.	Fatty acids taken. Grams.	Melting-point.	Iodine absorption.	Stearic acid minus 0.005 gram. Gram.	Melting-point of deposit.	Stearic acid. Per cent.
Head	0.5212	34.8 <sup>5</sup>	67.7	0.0452	67.8	8.67
"	1.0481			0.0993	66.2	9.47
Ham	0.5006	34.6	61.6	0.0438	67.5	8.74
"	1.0044			0.0906	67.3	9.02
Breast	0.5152	36.8	64.2	0.0610	67.2	11.84
"	1.0219			0.1114	66.8	10.90
Flare	0.4936	40.0	52.8	0.0774	66.5	15.70
"	1.0096			0.1450	67.2	14.40
Back	0.5002	35.6	67.9	0.0430	67.0	8.59
"	0.9998			0.0910	66.5	9.2
Flare from another pig :						
	1.5221			0.1940	67.2	12.70
	1.1320			0.1386	67.0	12.24

It will be observed that the melting-points of the deposits obtained were in all cases slightly lower than that of pure stearic acid, but a mere trace of liquid fatty acid would be fully sufficient to account for the depression.

Assuming that the iodine number measures only oleic acid, and that 100 parts of the latter absorb ninety parts of iodine, it is easy to calculate the percentage of stearic acid in the saturated fatty acids contained in the total fatty acids from the fat of the animal referred to. On making this calculation it is found that the following are the percentages of stearic acid in the saturated fatty acids: Head, 35.0 per cent.; ham, 28.1 per cent.; breast, 39.6 per cent.; flare, 36.4 per cent.; back, 36.1 per cent.

It follows that in the case of this particular animal, at least, the variation in the consistency of the fat from various parts was almost entirely due to fluctuations in the amount of oleic acid.

*Stearic Acid in Fat from Different Parts of the Same Sheep.*—The different specimens of fat were taken from a Scotch sheep eighteen months old :

## XVIII.

Part of sheep.	Fatty acids taken. Grams.	Iodine No. of fat.	Melting point of fatty acids.	Stearic acid minus 0.005 gram. Gram.	Percentage of stearic acid.
Back	0.5280	61.3	41.4	0.1310	24.8
Neck	0.5324	48.6	42.2	0.0876	16.4
Breast	0.7146	58.2	33.8	Very slight.	About one.
Ham	0.5100	50.6	40.8	No deposit after 2 days.	
Kidney	0.5030	48.16	45.6	0.1318	26.2
"	1.0175			0.2820	27.7

Calculating, as before, the percentage of the stearic acid in the saturated fatty acids we find: Back, 78.0 per cent.; neck, 36.0 per cent.; breast, 3.0 per cent.; ham, none; kidney, 58.0 per cent. The ham fat was liquid at ordinary temperature and that from the breast almost liquid.

In connection with these numbers, the following experiments may here find a place.

The molecular equivalent of the fatty acids from the sheep-kidney fat was found by titration with potassium hydroxide to be 271.6. The iodine number was 48.16, corresponding to 56.0 per cent. of oleic acid, assuming the whole of the iodine absorption to be attributable to oleic acid. The amount of stearic acid found being 26.2 per cent., there remain 17.8 per cent. for other saturated fatty acids. Assuming these to be palmitic, the calculated equivalent of the fatty acids is as follows:

$$\begin{array}{rcl}
 \text{Oleic acid, } 0.56 \times 282 & = & 157.92 \\
 \text{Stearic " } 0.262 \times 284 & = & 74.71 \\
 \text{Palmitic " } 0.178 \times 256 & = & 45.57 \\
 \hline
 & & 277.90
 \end{array}$$

A very fair approach to the 276.1 directly determined.

## XIX.

## DETERMINATION OF STEARIC ACID IN MISCELLANEOUS FATS.

	Taken.	Iodine No.	Stearic acid minus 0.005 gram. Gram.	Percentage in fatty acids.
Beef-stearine	0.3024	....	0.1516	50.19
"	0.4174	....	0.2131	51.05
Oleomargarine	1.0107	....	0.2295	22.00
"	0.5192	....	0.1104	21.26
"	1.1100	....	0.2630	23.6
Margarine 1	1.0035	....	0.2495	24.8
" 2	0.5000	....	0.0586	11.72
Horse kidney-fat	0.701	85.4	No deposit.	

	Taken.	Iodine No.	Stearic acid minus 0.005 gram. Gram.	Percentage in fatty acids.
Cotton 'stearine'	0.9945	....	0.0334	3.3
Stillingia tallow		22.87	No deposit.	
Cocoa-butter	1.0168	....	0.4064	39.9
"	0.9548	....	0.3878	40.6
Maize oil	5.4186	....	No deposit.	
Almond oil	5.0236	....	No deposit.	
Olive oil	5.5558	....	No deposit.	
Earthnut oil	1.0648	....	0.0751 (M. P. 67° C)	7.00

## XX.

*Examination of Lard Crystals Separated from Ether.*—It is well known to those who are accustomed to test for beef stearine in lard, that the form of the crystals obtained from pure lard is subject to considerable variation. While from some lards (the softer kinds) nothing but broad plates with pronounced chisel-shaped ends are obtained, from the harder kinds (flare lard) bunches of more pointed, though still chisel-edged, broad needles, crystallize. When the crystals are repeatedly recrystallized from ether, they as a rule become more and more needle-like, until they are practically undistinguishable from beef stearine crystals. One of us illustrated this point some time ago, before the Society of Public Analysts, by the exhibition of a large number of photo-lantern slides. After finding the remarkable differences in the amounts of stearic acid contained in various parts of the fat of the same pig, stated above, we thought that determinations of stearic acid in lard crystals might throw light upon this subject. No one as yet has attempted to explain the cause of the difference between the shapes of lard crystals and of beef stearine crystals, and it is not known whether the phenomenon is due to different isomerides, or simply to the proportion of stearic to palmitic or other acids contained in the deposits.

140 grams of a sample of flare lard, with an iodine absorption of 57.5 and a stearic acid contents of 16.11 and 16.05 per cent. in the fatty acids, were dissolved in a liter of warm ether. This is nearly the proportion of ether to lard generally employed in Stock's mode of working the Belfield test. Next morning there was an abundant deposit of crystals, showing the characteristic chisel-shaped ends. The crystals were separated, a small por-

tion saponified and the free fatty acids obtained. They were found to contain 32.4 per cent. of stearic acid. The ethereal solution, poured off from the crop of crystals, was evaporated, and part of the resulting fatty residue was decomposed to obtain free fatty acids. These contained only fifteen per cent. of stearic acid.

The main crop of crystals was then recrystallized from ether. The crystals were now needle-shaped, but had still distinct chisel-shaped ends. The fatty acids obtained from these contained 47.6 per cent. of stearic acid, while the fatty acids obtained as before from the second solution contained 17.23 per cent. stearic acid.

For a third time the crystals were crystallized from ether. The percentage of stearic acid had now risen in the fatty acids from the crystals to fifty-nine per cent., while the fat in solution contained 33.2 per cent. This third crystallization was, in form, hardly distinguishable from beef stearine crystals.

It can hardly be doubted, from a consideration of these results, that the form of the beef crystals is solely due to a larger proportion of stearic acid, than can be obtained from a pure lard by a single crystallization. When it is considered that pure lard contains, as far as our results go, not more than about fifteen per cent. of stearic acid, while beef stearine contains fifty per cent., it is intelligible, that from a beef-stiffened lard a deposit with a larger percentage of stearine is likely to result than from lard alone. At the same time the subject is quite worthy of a much more extended investigation.

The results also show that very many crystallizations would be required to separate the glycerides of palmitic and stearic acids fairly completely, as has been pointed out by Heintz many years ago.

## XXI.

*Examination of Samples of Butter.*—We have made considerably over one hundred determinations of stearic acid in butter fatty acids, utilizing for this purpose the fatty acids remaining behind in the Reichert method. In the large majority of cases no deposit at all, or only a very minute quantity separated from

the stearic alcohol. In some cases, however, phenomena apparently of supersaturation, occurred. Occasionally on examining the flasks after opening the ice-chest in the morning, the solution was perfectly clear, but after shaking the contents and leaving them for some time longer in the ice, a small, but increasing, crystallization formed. We have not quite concluded our investigation into the cause of this phenomenon, and as the question of the examination of butter, with a view to distinguish it from margarine mixtures, is of very great practical importance, we propose to deal with this part of the subject in a separate communication. Inasmuch as all constants which are now utilized for the discovery of admixtures with butter-fat, are occasionally breaking down, it would be a matter of obvious importance, if a constituent which is never absent from butter substitutes, *viz.*, stearic acid, could be shown to be absent from butter-fat, or to occur in it only in minute quantities. Analysts would then for the first time be in a position to distinguish absolutely between pure and adulterated butter. For the purpose of the investigation we would thank those of our colleagues who take an interest in the subject to kindly furnish us with small samples of undoubtedly genuine butters, normal and abnormal, together with their results of analysis, including any or all of the following : Reichert number, insoluble fatty acids, refractive index, together with any details that may be of interest or importance.

## XXII.

*On the Abnormal Behavior of Palmitic Acid Obtained from Japan Wax.*—Japan wax, consisting or supposed to consist mainly of palmitine with free palmitic acid, is considered to be a ready source of palmitic acid. We prepared a quantity of the acid from Japan wax, possessing apparently all the properties of palmitic acid. On making mixtures of this acid with known amounts of stearic acid, we were surprised to find that only a part, or none at all, of the added stearic acid could be obtained by crystallization from stearic alcohol, as the following figures will show :

Stearic acid. Gram.	Japan-wax acid. Gram.	Time of standing.	Stearic acid found. Gram.
0.1440	0.5	8 days	0.0438
0.2500	0.5	12 hours.	0.1542
0.0200	0.5	12 hours, turbidity only.	
0.2000	0.5	60 hours.	0.1800
0.4000	0.5	12 hours.	0.3800
0.2370	0.5	4 days.	0.2217
0.1500	0.5	4 days.	Turbidity only.
0.1000	0.100	12 hours.	Very slight precipitate.
0.0500	0.1	3 days.	" " "
0.05	0.2	"	" " "
0.025	0.225	"	" " "
none.	0.5	2 days.	none.

Without extended investigation it is impossible even to guess at the reason of the abnormal behavior of Japan-wax acids. Whether they combine with the added stearic acid, or cause the latter to be etherified by the alcohol, we are unable to say. The whole subject of Japan wax is quite worthy of investigation, as the statements made concerning it are somewhat contradictory. In any case, the failure to apply our method to Japan-wax acids does not directly bear upon the question of determination of stearic acid in ordinary fats and oils, in which we are quite satisfied that acid can be determined with reasonable accuracy.

The principle underlying the method described may be applied also to the determination of other fatty acids, such as palmitic and arachidic. In the former case the results would of necessity be less exact on account of the far more considerable solubility of palmitic acid and the greater correction number to be applied. For arachidic acid, on the other hand, the method ought to do good service, as it may safely be assumed that its solubility is far less than that of stearic acid. We hope to recur to the subject at some future time.

To summarize in a few words the method which we recommend :

Prepare a supply of alcohol saturated with pure stearic acid, or with stearic acid containing not much palmitic acid, at 0°C. Dissolve from one-half to one gram of the fatty acid mixture to be examined, if these are solid, or about five grams if fluid, in about 100 cc. (exact measurement is not necessary) of stearic alcohol. Leave in an ice bath over night, agitate the mixture next morn-



ing and allow to stand in ice for a short time, filter off while the mixture remains in ice, wash with stearic alcohol at  $0^{\circ}$  C., dry and weigh. Determine the melting-point of the product, which should not be much less than  $68.5^{\circ}$  C.

11 BILLITER SQUARE, LONDON, NOV. 23, 1896.

## THE DETERMINATION OF SOLID FATS IN COMPOUND LARDS.

BY GEORGE F. TENNILLE.

Received December 11, 1896.

IN March, 1896, there appeared in this Journal an article by J. H. Wainwright entitled, "The Determination of the Solid Fat in Artificial Mixtures of Vegetable and Animal Fats and Oils."

Samples of compound lards had been submitted to the United States laboratory for the determination of the relative proportion of their constituents in order that the claim of the exporters for "drawback" of duties paid on one of the constituents might be verified, and the paper consisted in a description of a mechanical process which had been adopted by the United States laboratory for use in such determinations.

Though no great claim for accuracy in results or of scientific principles involved was made yet the conclusion arrived at was that the process would give correct results to within about one and one-half per cent.

Having been connected with one of the companies interested in the collection of this "drawback" of duties paid on the oleostearine used in compound lard, and having personally supervised the making of the lard which was sent to the United States laboratory for analysis, and hearing that the result obtained by the chemist often fell short of the actual amount of oleostearine which I knew to be contained in the samples, I made a great many trials of the process and came to the conclusion that, though under certain conditions it might give concordant and fairly accurate results, it could not be relied upon at all under certain other conditions.

I have selected a series of ten from the many analyses which were made with a view of showing in a rather exaggerated manner perhaps the possible results when the test is carried out under those conditions which prohibit accuracy.

The process was carried out by me essentially as described in this Journal, 18, 259, except in two particulars.

Firstly, the sample after the preliminary melting and slow cooling to 75° F. was allowed to stand at exactly that temperature for twenty-four hours before subjecting to pressure, instead of "standing over night at ordinary temperature," as described by the author of the process, and secondly, twenty-five grams of the sample instead of fifty were used in the screw press.

These ten samples each contained twenty per cent. oleostearine and eighty per cent oil.

No. 1.		Grams.
Oleostearine.	Titre 50.6° C.....	20
Cotton-seed oil.	A very heavy bodied oil.....	80
No. 2.		
Oleostearine.	Titre 50.6° C.....	20
Cotton-seed oil.	A moderately heavy bodied oil.....	80
No. 3.		
Oleostearine.	Titre 50.6° C.....	20
Cotton-seed oil.	An ordinary oil.....	80
No. 4.		
Oleostearine.	Titre 50.6° C.....	20
Cotton-seed oil.	An ordinary oil.....	80
No. 5.		
Oleostearine.	Titre 50.6° C.....	20
Cotton-seed oil.	A very light bodied oil.....	80
No. 6.		
Oleostearine.	Titre 46.2° C.....	20
Cotton-seed oil.	The same oil as in No. 1 .....	80
No. 7.		
Oleostearine.	Titre 46.2° C.....	20
Cotton-seed oil.	The same oil as in No. 2 .....	80
No. 8.		
Oleostearine.	Titre 46.2° C.....	20
Cotton-seed oil.	An ordinary oil.....	80
No. 9.		
Oleostearine.	Titre 46.2° C.....	20
Cotton-seed oil.	An ordinary oil.....	80
No. 10.		
Oleostearine.	Titre 46.2° C.....	20
Cotton-seed oil.	The same oil as in No. 5 .....	80

The following are the percentages of solid fat which were obtained by Wainwright's method on these samples :

**DETERMINATION OF SOLID FATS IN COMPOUND LARDS. 53**

Samples		Per cent.
No.	1.....	28.14
"	2.....	26.83
"	3.....	21.07
"	4.....	23.77
"	5.....	18.10
"	6.....	21.71
"	7.....	19.43
"	8.....	16.77
"	9.....	16.10
"	10.....	13.13

Cotton-seed oil, as every one is aware who has ever handled it to any great extent, varies in the relative amounts of its chief constituents.

For instance, a natural sample of cotton-seed oil may be of such character that it will remain a limpid liquid for any length of time at a temperature of 32° F.; another oil may deposit stearine at as high a temperature as 80° F., may be a viscous liquid at 65°, and a hard brittle fat at 32° F. Such oils, of course, are unusual and are extremes not often met, but they do occur and may come to the refiner and be used in the manufacture of his compound lard.

Again, oleostearine differs in its constitution, but here the differences are due to the process of its manufacture and not to the processes of nature as in the cotton-seed oil.

The temperature at which the oleo stock is pressed and the amount of pressure applied, which variations may be due to the state of the markets for oleo oil and oleostearine, or due to the carelessness of the workman, effect the composition, and therefore the hardness of oleostearine.

In the examples given above I have chosen purposely an unusually hard stearine and one of unusual softness; an extremely heavy bodied cotton-seed oil, a moderately heavy bodied cotton-seed oil, four ordinary cotton-seed oils, and one of unusual light body.

On running titre tests on the cakes obtained in the screw press it was found that they were within a fraction of a degree in each case of the titre of the oleo which had been used in the samples, thus showing that the pressure in the screw press had been sufficient to insure accurate results if the suppositions upon which the process was based were correct; namely, that from a

mixture of oleostearine and cotton-seed oil, which had been melted and cooled and allowed to stand at a moderate temperature for some hours, all of the oleostearine would crystallize out, and all of the oil remain a liquid.

The cakes were also tested qualitatively for cotton-seed oil and were found to contain it. The oil drained off from the pressing was also tested for beef fat and found to contain it.

It would seem from an examination of the above results that a cotton-seed oil which had a very heavy body, that is, which would easily deposit stearine at ordinary temperatures, when subjected to this process will add some of its stearine to the oleostearine crystallizing from the mixture and render the results too high; that an ordinary cotton-seed oil gives up very little stearine to the cake but has a tendency to dissolve or keep in solution a portion of the beef fat, a greater portion the softer the beef fat; that a light bodied cotton-seed oil, having comparatively very little stearine in its composition and being capable of dissolving a greater amount than an ordinary oil, has a tendency to do so, and keeps more of the beef fat in solution and the more the softer the beef fat.

A very hard oleostearine has a tendency to make the cakes heavier, owing to the difficulty in pressing out the last portions of the oil.

A very soft oleostearine has a tendency to make the cakes lighter, for a portion of the liquid glycerides contained in it may be pressed out with the oil.

It is evident then, that this process of determining the relative amounts of the constituents of compound lard cannot be relied upon. It may, indeed, under ordinary conditions, give results which may very easily be within one and one-half units of the true percentage, but if the conditions be at all varied, and they are very likely to be varied, the results may be at least seven or eight per cent. too high or low.

## ESTIMATION OF BORIC ACID IN FOODS.

BY L. DE KONINGH.

Received November 13, 1896.

**T**HE estimation of boric acid, at one time very troublesome, has become quite an easy matter since the discovery that it may be accurately titrated in presence of glycerol with phenolphthalein as indicator. To apply the process to articles of food, (and I will confine myself for the present to milk and uncooked eggs,) some few precautions must, however, be taken.

Boric acid is seldom used alone, but mostly in admixture with borax, a mixture of three parts of the acid with one part of ground borax, constituting the article known as *glacialine*. In practice it is, however, in my opinion, not necessary to make a distinction between the acid and its sodium salt, as, both are no doubt equally harmless in small quantities; but if the amount of either reaches one per cent. or more the time has come for a protest.

When testing uncooked eggs (the entire contents beaten up) for boric acid, I take five grams of the sample, add one drop of sodium hydroxide (1 : 1), dry, and finally incinerate. The char is then powdered, boiled with water, and the residual black mass again burnt. The ash is also boiled with water and the two solutions are united. The liquid is now faintly colored by methyl orange and tenth-normal sulphuric acid is added until a faint pink is obtained. The solution is now boiled for a minute to expel carbon dioxide, cooled, mixed with one-half of its bulk of glycerol, and titrated with tenth-normal sodium hydroxide, with phenolphthalein as indicator. Although it is now admitted that in presence of glycerol the amount of acid may be calculated from the number of cubic centimeters of sodium hydroxide used, I prefer to check my sodium hydroxide with pure crystallized boric acid, using about the same quantity as present in the sample, and mixing this up with exactly the same amount of glycerol and water. Working in this manner the estimation of boric acid is, as regards accuracy, second to none.

It must, however, be remembered that eggs contain a small quantity of alkaline phosphates, and that phosphoric acid behaves somewhat like the boric acid. A method of removing this acid has already been proposed and is based on the insolu-

bility of calcium phosphate and the *comparatively* large solubility of the borate. I find, however, that in uncooked eggs there is just enough phosphoric acid to account for three cc. tenth-normal sodium hydroxide, when working on five grams of sample, so I now propose to deduct three cc. of sodium hydroxide from the number of cubic centimeters taken by the sample. I scarcely need point out the necessity of proving the acid by the alcohol test. As a rule the presence may be ascertained by simply stirring some of the sample with a drop of sulphuric acid and a little spirits of wine and then setting fire to it.

When dealing with milk I allow one cc. of sodium hydroxide for every ten grams of the sample. If the amount of acid is, as usual, very small, no particular accuracy can be claimed for the process; but if present in larger and, consequently harmful quantity, the results are all that may be desired.

LONDON, ENG., JUNE, 1896.

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## A STUDY OF THE CLARIFICATION OF SUGAR CANE JUICE.<sup>1</sup>

BY J. L. BRESON.

Received December 3, 1896.

THE clarification of the cane juice, so important a factor in the manufacture of sugar, is practically the same in method as that in use by the planters of Louisiana one hundred years ago. The method consists in the addition of slaked lime or milk of lime to the cold juice until neutrality or slight alkalinity is reached; then the temperature of the mass is raised nearly to boiling, when a coagulum forms and is carried to the surface by the upward motion of the liquid, and there forms a thick dark green scum called "the blanket." This is removed by skimming, and calcium superphosphate solution (called clariphos), is added until the juice begins to brighten in color. The method is, in the main, an empirical one, the nature of the bodies removed and the chemical changes involved therein not being understood. The practical sugar boiler has virtually no facts to guide him in this important branch of his work. It was therefore the object of this investigation to compare the juice expressed by the mill with that obtained from the same large sample of cane obtained by

<sup>1</sup> This work was done in the laboratory of the Audubon Sugar School, New Orleans, which institution was discontinued last July.

the process of diffusion with hot water. Also to compare these juices before and after clarification, and to study the products so removed. The methods of analyses used were those adopted by the Association of Official Chemists. The total proteids and albuminoids were obtained by multiplying the total and albuminous nitrogen by the factor 6.25, the difference being termed amids. The "gums" or non-nitrogenous solids not sugars, were obtained by subtracting the total proteids and ash from the "solids not sugars." Since the diffusion juice is more dilute than the mill juice, the results of the former were calculated to the same total solids of the mill juice for the sake of easy comparison. These analyses were made in duplicate throughout. Below is given the results of these analyses :

## ANALYSIS I.

	Total solids.	Sucrose.	Glucose.	Solids not sugars.	Purity co-efficient.	Ash.	Gums.	Total proteids.	Albuminoids.	Amids.
Mill juice.....	14.9	10.8	2.03	2.07	72.5	0.413	1.385	0.292	0.099	0.193
Diffusion juice .....	14.9	11.4	1.87	1.63	76.5	0.448	0.93	0.224	0.065	0.179
Clar'fi'd diffu'n juice	14.9	11.3	1.97	1.63	75.9	0.456	0.97	0.204	0.056	0.148

By comparing the juice from the mill with that obtained by diffusion with hot water, it will be seen the latter contains less solids not sugars, less total proteids, less albuminoids and amids than the mill juice. This would indicate that the hot water had, during the process of diffusion, coagulated and left behind in the bagasse about one-third of both the albuminoids and gums, in which case analyses of the bagasse from these two sources should show more albuminoids and gums in the diffusion sugars. Estimation of the gums was not attempted, but estimation of the total proteids in the two bagasses showed an excess in that from the diffusion, as will be seen below :

## ANALYSIS II.

	Per cent.
Bagasse from mill, proteids .....	1.146
Bagasse from diffusion process, proteids.....	1.731

This analysis was repeated with mill and diffusion bagasse of another variety of cane, showing as before a larger percentage of proteids in the latter.

By comparing the clarified with the unclarified diffusion juice it will be seen that there was a further, but much smaller, removal of the albuminous bodies by the action of lime and heat in the process of clarification. But there was a slight increase in ash and what is estimated as gums, attended by a lowering of the coefficient of purity of the juice. The increase in ash doubtless accounts for the increase in what is termed gums, for the lime had combined with the free acids in the juice, most of which acids identified in the juice form soluble compounds with lime. Then it is a well known chemical fact that hot alkaline solutions will decompose amids with the liberation of ammonia, forming the alkaline salts of the acid of the amid. This would further augment the lime salts in the juice. The decrease in amids in the clarified juice in this case would indicate that this decomposition of the amids had taken place during the heating and skimming. If the juice were sufficiently alkaline and the heating prolonged, we should expect the albuminoids to be broken down into their constituent compounds, reducing sugars, amids, etc., and the latter broken up into ammonia and lime salts of the acid of the amid. This would decrease the albuminoids, as is true in the above case, as well as increase the lime salts in solution. It is clear that excessive use of lime and heat would decrease the purity of the juice, as is noticed in this case. These analyses were repeated with five different kinds of cane, each time showing results similar to the above. This lowering of the purity of the juice by clarification was doubtless due to the presence of an excess of lime due to the solution of the larger particles of lime during the heatings and skimmings, for an analysis of the settlings in the bottom of the clarifying tanks showed about fifty per cent. of lime. This trouble, of course, could be remedied by using lime which had been ground to an impalpable milk with water in a mill. This would approximate a true solution. Lime-water cannot be used on account of the dilution it effects. The amount of ash in the clarified juice depends upon the original acidity of the juice and the amount of calcium superphosphate added after skimming. If more be added than is required to remove the free lime, there might be a lessening of the ash, but this would again set free the acids in the juice,



which might cause considerable inversion during the subsequent heatings and evaporations.

Below is given the analysis of the products removed by the clarification :

ANALYSIS III. OF SKIMMINGS.

	Per cent.
Ash .....	26.84
Proteids.....	15.52
Gums and acids .....	57.52

The relatively small quantities of albuminoids in this coagulum would indicate that some of these bodies had been broken down by the clarification, as was previously suggested, and the presence of so large quantities of ash and non-nitrogenous bodies would indicate the formation of lime compounds. Upon comparing the three juices in Analysis I it is clear that the greatest purging of the juice was effected by heat alone during the process of diffusion, removing a third of the albuminoids and gums in the juice, the lime or heat in the clarification removing a further portion of the albuminoids, but increasing the non-nitrogenous bodies of the juice. What would be the relative effect if lime were added first and then heat applied? Which is the clarifying agent, lime, or heat, or both? In order to throw light upon these questions the following experiment was performed: To one liter of cold mill juice, clear lime-water was slowly added. After the acidity of the juice had disappeared (about ten cc. were required), a dark greenish precipitate appeared and continued to form as the lime-water was added until a faint alkalinity was reached, requiring 190 cc. more of the lime-water. This precipitate was carefully collected, dried at 100° C., weighed and analyzed. Then a few drops of calcium superphosphate solution were added until the juice began to brighten, in order to remove the small quantity of free lime. The juice was then heated for twenty minutes to 90°–95° C., when a small coagulum was formed. This was collected, dried, weighed and subjected to analysis. Many sugar houses pass sulphur dioxide into their juices before clarifying with lime and heat. In order to see if sulphur dioxide removed any bodies which lime and heat would not, a portion of the above juice was saturated with sulphur dioxide gas and heated. The juice was bleached, but no further

precipitate was formed. But this does not show that sulphur dioxide will not reduce certain organic bodies to compounds removable by lime and heat which would not otherwise have been removed by these agents. No experiments could for lack of time be made to settle this important point. Below is given the analysis of the juice before and after the lime-heat clarification :

ANALYSIS IV.

Mill juice.	Total solids.	Sucrose.	Glucose.	Solids not sugars.	Purity coeff. cent.	Ash.	Gums.	Total proteids.	Albuminoids.	Amids.
Unclarified ....	14.9	11.32	2.54	1.04	75.9	0.309	0.602	0.131	0.109	0.0224
Clarified .....	14.9	11.91	2.37	0.72	79.4	0.301	0.365	0.062	0.041	0.021

ANALYSIS V. OF THE PRODUCTS REMOVED BY CLARIFICATION.

	Ash.	Albumi- noids.	Gums.
Precipitate with lime, weight in 100 grams juice, 0.266 gram .....	20.6	18.06	61.54
Coagulum from heating afterwards, in 100 grams juice, 0.025 gram ..	11.5	37.28	51.25

The clarified juice was much clearer and lighter in color than the unclarified. By comparing the constituents of the two juices one by one it will be seen that there is a marked improvement, due to clarification when the process is carefully carried out. The lime-heat clarification has removed over half of the albuminoids, and nearly half of the gums, resulting in a loss of about one-third of the solids not sugars, and an increase in the coefficient of purity of about four per cent. of the juice. By applying the results in Analysis V to those in Analysis IV, it will be seen that the lime alone, when added first, has removed about forty-eight per cent. of the entire albuminoids, and about thirty-six per cent. of the entire gums in the juice, whereas heat alone applied first (Analysis I) removed about thirty-five per cent. of the albuminoids and forty per cent. of the gums. From this it would appear that lime is in general the more effective purging agent, removing decidedly more of the albuminoids, but less of the gums than heat. From Analysis V it will be seen that of the total organic matter removed, nearly ten-elevenths were removed by the lime. Of the albuminoids removed, four-fifths were removed by the lime, and of the gums nine-tenths, the remaining portions of both the albuminoids and gums being removed

by the heat. It is quite clear that the lime has formed insoluble compounds with both the gummy bodies and the albuminoids, the latter forming calcium albuminates, probably similar to the better known copper albuminates. But the lime does not combine with all of these bodies in the juice, or if it does the compounds are soluble. The lower percentage of ash in the coagulum would indicate that if such soluble but coagulable compounds were formed, they were of a different nature, containing less lime. The albuminoids and gummy bodies in cane juice may then be divided into three classes: (*a*) Those which form insoluble compounds with lime, (*b*) those which are precipitated by heat, and (*c*) those which are not rendered insoluble by both lime and heat, the gummy bodies of class *c* being precipitable by nitrate of mercury and the albuminoids by copper hydroxide. Class *c* constitutes nearly one-half of these bodies in the cane juice. It is the further work of the sugar chemist to discover some cheap non-poisonous agent which will remove this class of bodies from the cane juice.

### A NEW FORM OF PYKNOMETER.<sup>1</sup>

By J. C. BOOT.<sup>2</sup>

Received November 9, 1896.

OF all the different forms of pyknometers, Fig. 1 represents the one that is probably most generally used.

Working with this form in a room where the temperature is much higher than the normal, there is one difficulty to contend with, which is, that in the time it takes to dry and weigh the pyknometer the liquid is continuously running out of the capillary tube in the stopper.

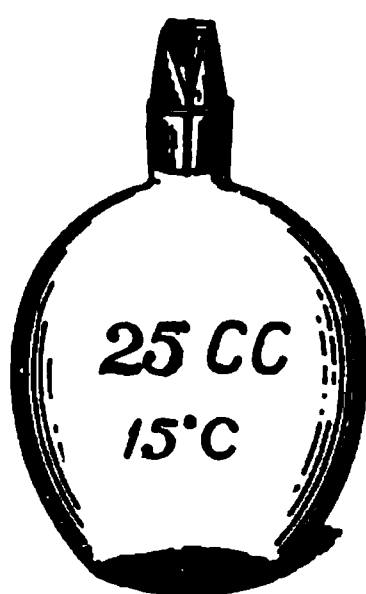


Fig. 1.

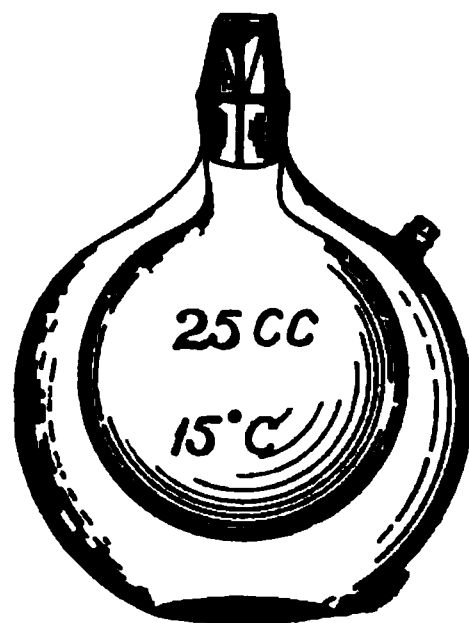


Fig. 2.

For the purpose of making accurate specific gravity determi-

<sup>1</sup> *Chem. Ztg.*, 1896, 20, 63.

<sup>2</sup> Read before the New York Section of the American Chemical Society, Nov. 6, 1896.

nations under such conditions, that is to say, when the temperature of the balance room is high, I have constructed a pyknometer with double walls, as shown in Fig. 2, in which the space between the two walls is carefully exhausted.

The apparatus is used in the following way:

Take for example a pyknometer of twenty-five cc. capacity and a normal temperature of  $15^{\circ}$  C.

Of the liquid, whose specific gravity is to be determined, we take about fifty cc. in a small flask and cool down to about  $12^{\circ}$  to  $13^{\circ}$  C.; a thermometer divided into  $\frac{1}{10}^{\circ}$  or  $\frac{1}{5}^{\circ}$  is used for noting the temperature.

After shaking the contents of the flask, wash out the pyknometer with about five cc. of the liquid, throw away these five cc. and then run in about twenty cc. The temperature of the liquid in the pyknometer will probably be about  $14^{\circ}$  C.

This twenty cc. are poured back into the flask and again about twenty cc. of the liquid are poured into the pyknometer. The temperature will now be about  $14^{\circ}.2$  C.

This pouring of the twenty cc. into the pyknometer and then back into the flask is continued until the temperature of the liquid is  $15^{\circ}$  C.

We then fill up the pyknometer until it overflows and put in the stopper.

The apparatus can now be carefully dried and weighed without danger of any of the liquid running out of the capillary tube.

In this pyknometer, as shown in Fig. 1, it often happens that when drying, the simple pressure against the glass sides causes the liquid to run out through the capillary tube. Naturally this is impossible with my pyknometer.

The apparatus has proved very satisfactory. It weighs about thirty grams, and is made by Eimer & Amend, New York, and by Christ Kob & Co., Stützerbach, Germany.

# THE CAFFEIN COMPOUND IN KOLA.<sup>1</sup>

BY JAMES W. T. KNOX AND ALBERT B. PRESCOTT.

Received December 19, 1896.

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## HISTORICAL.

Although the literature of kola extends back more than three hundred years, its chemical history is comparatively recent and may be briefly summarized as follows :

To Attfield<sup>2</sup> belongs the credit of proving that kola contains caffein ; his work was done at the instance of Dr. Daniell,<sup>3</sup> who had made quite a study of the uses of kola among the natives of Western Africa, and who suspected from its physiological effects

<sup>1</sup> From the Proceedings of the American Pharmaceutical Association, 1896. Communicated by the authors.

<sup>2</sup> *Pharm. J. Trans.*, 1865, (2) 6, 457.

<sup>3</sup> *Pharm. J. Trans.*, 1865, (2) 6, 450.

that it contained a stimulating principle similar to that of coffee and tea. Their supply of material was limited and they seem to have carried their investigation into its chemistry no further.

In 1882 Heckel and Schlagdenhauffen<sup>1</sup> reported a more complete analysis of kola differing especially from that of the earlier workers in that it showed, in addition, the presence of theobromin and tannin. Heckel also noticed that a body was present which seemed to him to present considerable analogy to cinchona red, and he applied the name "kola red" (rouge de kola) to it. This, he afterwards found, gave a sublimate of caffein upon heating sufficiently, and he supposed the alkaloid to be retained mechanically, although he was unable to remove it by prolonged treatment with chloroform.

Knebel,<sup>2</sup> working in the Pharmaceutical Institute at Erlangen under the direction of Prof. Hilger (now at Munich), took up the investigation at this point in 1892, and isolated a tannin-like body to which he ascribed the formula  $C_{12}H_{12}(OH)_6$ , and which he named "kola red." This is not to be confounded with the kola red of Heckel, for Knebel considered Heckel's product an indefinite mixture, or rather an impure form of a glucoside which he (Knebel) believed to be present in kola, and which he believed to be composed of equal molecular proportions of caffein, glucose, and "kola red." This glucoside he called "kolanin," and, although he had only the dry seeds of kola to work upon, he inferred, from the proportions of caffein and glucose found therein, that in the fresh seeds no caffein was free. He inferred that the whole was combined in the glucoside, which under the influence of a diastatic ferment (which he isolated), with air and moisture, was partially decomposed, during the process of drying, into its component parts.

This hypothesis also seemed to explain why different workers, using different samples of the drug, had failed to get uniform results in the yield of caffein, for only the free alkaloids are removed by the immiscible solvents usually employed in assaying, combined alkaloids remaining behind. . Different conditions in drying would give a variable extent of decomposition of this

<sup>1</sup> Heckel and Schlagdenhauffen, 1882 : *Repert. de Pharm.*, p. 163.

<sup>2</sup> E. Knebel, 1892 : *Apoth. Ztg.*, 7, 112.

(hypothetical) glucoside, and consequently afford discordant results in assaying.

Prof. Dr. Hilger<sup>1</sup> had noticed the apparent untrustworthiness of the usual assay methods in the examinations of cacao as well as of kola and was led by Knebel's results to investigate the chemistry of cacao, working at Erlangen. He succeeded in separating a glucoside from cacao analogous to the one Knebel supposed to be present in kola, and which yielded on hydrolysis with dilute mineral acids, theobromin, dextrose, and cacao red,  $C_{17}H_{19}(OH)_{10}$ , similar to kola red. The dextrose formed with phenylhydrazin a glucosazone of melting-point  $204^{\circ}$  C. Later,<sup>2</sup> at Munich, he applied the same and similar methods to kola, using the fresh seeds, and obtained a body, the "kolanin" of Knebel, yielding caffein, dextrose, and kola red on decomposition with dilute mineral acids, or diastatic ferments. He also describes in his paper his method for separating the ferment of kola, these details having been omitted from Knebel's original article.

Prof. Dr. Hilger has also kindly sent us the Inaugural-Dissertation<sup>3</sup> of Schweitzer for which we here make grateful acknowledgment. Schweitzer continued the work on kola and cacao, begun by Knebel and Hilger, verifying their results. His work on the (supposed) glucoside of kola indicates the combination of one molecule each of caffein and kola red, and three of dextrose, instead of one of each as claimed by Knebel. He proposes the formula  $C_{46}H_{58}N_4O_{21}$  for "kolanin."

Another feature of his work on kola is, that while in the free alkaloids the proportion of caffein is to theobromin as 98.8 to 1.2, in the glucoside, he found it to be 80.3 of caffein to 19.7 of theobromin.

Of American workers, Schlotterbeck<sup>4</sup> and Topping<sup>5</sup> have done good service; Dohme and Engelhardt<sup>6</sup> have published reports of comparative assays of African and West Indian kolas. They found the African superior.

<sup>1</sup> A. Hilger, 1892: *Apoth. Ztg.*, 7, 469.

<sup>2</sup> A. Hilger, 1893: *Dtsch. Vierteljahresschrift f. öffentl. Gesundheitspflege*, 25, 559. Drittes heft.

<sup>3</sup> Carl Schweitzer, 1895: Inaugural-Dissertation zur Erlangung der Doktorwuerde, Munich.

<sup>4</sup> Kola: Monograph by J. O. Schlotterbeck, Detroit, 1894.

<sup>5</sup> C. O. Topping, 1894: *Proc. Am. Pharm. Ass.*, p. 178.

<sup>6</sup> Dohme and Engelhardt, 1896: *Am. Drugg.*, p. 12.

Other recent contributors are Kilmer, whose paper is principally a compilation and Jean,<sup>2</sup> who examined a number of commercial preparations of kola, *i. e.*, its fluid extracts, tinctures, and wines.

A partial plant analysis of kola was made last year by one of us, with Prof. Schlotterbeck.<sup>3</sup>

#### THE SAMPLE.

Through the liberality of Messrs. Frederick Stearns & Co., Manufacturing Pharmacists of Detroit, Michigan, we were supplied with a large original package of kola nuts, just as imported by them from West Africa. The basket had not been opened, and the seeds were perfectly fresh, and were fine specimens. The best of these were selected, and as a means of preservation they were sealed up air-tight in clean and dry glass-stoppered jars. In about one-half the number of jars the air was displaced by dry carbon dioxide, and in a few others the red and white seeds were put up separately. That the carbon dioxide did not inhibit fungus growth, was shown by the appearance after five month's duration of a slight moldiness on some of the seeds put up in this atmosphere as well as on those preserved in air. This was not universally the case. At this time, after the expiration of nine months, we have several jars of the drug put up in exactly the same way, and at the same time in which the seeds are fresh and sound. Those preserved in carbon dioxide are somewhat paler, but internally are apparently unchanged, and a greater proportion of the seeds in this atmosphere, remained in prime condition, so that there would seem to be a slight advantage in its use. It is a rather remarkable fact that in those jars containing only red or only white seeds, there was no perceptible decomposition or fungus growth, and this regardless of the atmosphere used.

*Action of Solvents.*—When fresh kola seed is cut or bruised a chemical change immediately takes place, as shown by the rapid change of color of the cut surface from pink or cream-color to red-brown.

Desiring to avoid any decomposition of the drug in handling, a solvent was sought which would remove the active constituents

<sup>1</sup> F. B. Kilmer, 1896: *Am. J. Pharm.*, 68, 96.

<sup>2</sup> J. Jean, 1896: *Repert. de Pharm.*, (3), 7, 49.

<sup>3</sup> Knox and Schlotterbeck, 1895: *Analysis of Kola, Proc. Am. Pharm. Ass.*, p. 334.



without change. Water, absolute alcohol, ninety per cent. alcohol, fifty per cent. alcohol, ether, chloroform, benzene, acetone, ethyl acetate, dilute ammonia water, dilute potassium hydroxide solution, one per cent. hydrochloric acid, alcohol containing one per cent. of acetic acid, and glycerin, were the principal solvents tried. All were objectionable because the red coloration appeared almost immediately on contact of the cut surface of the drug with the liquid, coloring the solvent, if the coloring matter were soluble therein. Slicing the seeds under the surface of any of these liquids apparently neither retarded nor modified the formation of color.

Water was at first colored red, but gradually became turbid from precipitation of a portion of the matter at first dissolved; the alcohol of either strength gave a rich wine-red solution, which was permanent. The immiscible solvents removed only alkaloids and fat; both fixed and volatile alkalies developed an intense dark crimson color, changing to light scarlet on addition of excess of mineral acids, which change was accompanied by precipitation of a reddish flocculent substance; dilute acids heightened the color somewhat; glycerin seemed only to dehydrate the tissues without exerting solvent power.

*Action of Heat.*—This coloration has usually been ascribed to the activity of a diastatic ferment, and, therefore, recalling the action of heat on such bodies, it was decided to try the effect of sterilization on this drug. Accordingly a seed was sliced, the slices being received in boiling water. No coloration took place then or afterwards, a few seconds contact with the boiling water being sufficient to prevent its appearance. Further experimentation showed that up to  $60^{\circ}$  C. the heat augmented the production of color; from  $60^{\circ}$  to  $65^{\circ}$  it was somewhat retarded, and above  $65^{\circ}$  the slices retained their natural color.

On account of the starch present in kola, and for other reasons, the use of water was objectionable, so boiling alcohol was substituted successfully, and has been used exclusively by us for this purpose ever since. A temperature of  $45^{\circ}$  C. is sufficient when alcohol is employed to "coagulate the ferment," at least to prevent the coloration afterwards. Boiling chloroform and boiling acetone were each tried, but without successful results. Without

further discussion of the action of solvents, it may be remarked that, for pharmaceutical purposes and any others, when it is desirable to extract all the active constituents from kola with a single menstruum, our experience has shown that alcohol of not less strength than U. S. P. dilute alcohol is the most satisfactory agent.

*Action of Cold.*—It has been stated<sup>1</sup> that extreme cold seems to destroy the power of this ferment. An experiment, next described, seems to show that cold does not impair the potency of the ferment, but rather seems to preserve it. Two white kola seeds were sealed up in a dry bottle and immersed in a freezing mixture for three hours. On thawing, the production of the red-brown color was very rapid both upon cut and whole surfaces.

#### ASSAY OF KOLA.

*Common Causes of Error.*—Of the numerous methods proposed at various times by different workers for the assay of this drug, none has proven satisfactory and reliable. Many of these do not account completely for the free alkaloids of kola, and not at all for the combined alkaloids; others perhaps indicate pretty well the proportions of free alkaloids. Still, concordant results are not obtained, and the published assays of kola have a wide range of variation. Two reasons for these discrepancies have suggested themselves to us. First, insufficient knowledge of the properties of the combination bearing caffein has prevented the use of proper methods to secure complete liberation of the alkaloids from it; second, the caffein obtained is *weighed*, in a state of greater or less purity, varying with the method used and the care and judgment of the worker. It is not difficult to perceive how errors might thus be introduced.

We have worked out a plan of assay for kola especially intended to avoid these and some other common sources of error; it has been used by us in all the assays reported herein and in many others, and has given uniform and concordant results, higher than any we have yet seen. We offer it with a confidence based on experience.

*Volumetric Method for Caffein Determination.*—Before giving the details of manipulation for assay, it may be well to describe

<sup>1</sup> Kilmer, 1896: *Am. J. Pharm.*, 68, 104.

the volumetric method for the estimation of caffein which is substituted for gravimetric methods.

This new process, given by Gomberg<sup>1</sup> is based upon the very complete precipitation of caffein by Wagner's reagent from aqueous solutions when these are acidulated with mineral acids—a fact which seems to have been pretty generally overlooked by the text-books bearing upon the subject. This oversight is, no doubt, traceable to the fact that caffein, being soluble in water, with neutral reaction, and not forming salts permanent in water, is taken as free alkaloid for all tests in the wet way. Other alkaloids, for the most part, are taken in their salts, for reactions in solutions, their salts having the neutral reaction. Therefore the Wagner's reagent, like other reagents, was generally applied to the caffein solution without the presence of any acid, and under such conditions, it is true, as stated in the text-books, that "caffein is not precipitated by Wagner's reagent."

Gomberg recently investigated the subject at considerable length. Without entering into discussion of other features of his work, it may be stated briefly that he found that an aqueous solution of caffein, even so dilute as 1 to 8000, is precipitated by Wagner's reagent in the presence of mineral acid, and that the precipitate formed is constant in composition ( $C_8H_{10}N_4O_6HI.I_2$ ) in varying conditions of formation.<sup>2</sup> Having established these facts, practical application of them was made for the volumetric estimation of caffein. A short outline of the principal features of this method follows.

A definite volume of Wagner's reagent of known strength is added in excess to the measured caffein solution slightly acidulated with sulphuric or hydrochloric acid, and the clear liquid is decanted off after the precipitate has settled or is filtered through asbestos after five minutes' standing. The excess of iodine is titrated with decinormal sodium thiosulphate solution, using an aliquot portion of the filtrate. From this the number of cubic centimeters of decinormal Wagner's reagent can be calculated, which number multiplied by 0.00485 equals the weight of the anhydrous caffein.

We have had considerable experience with this process for

<sup>1</sup> This Journal, 18, 331.

<sup>2</sup> This Journal, 18, 350.

estimating caffein, as one of us (K.) furnished the original analytical data for Dr. Gomberg's paper, and we have employed it almost exclusively in the work upon the caffein compound since that time.

The table of results (p. 71) is reproduced from Gomberg's article. By way of explanation it may be said that solutions of caffein of respectively 0.25, 0.50, 0.75, and 1.00 per cent. strength were used, the acidulation was with sulphuric acid, and Wagner's reagent was employed in varying proportions, using a very slight excess over the theoretical amount, one and one-third times the theoretical amount, twice the theoretical amount, and one-half the theoretical amount. The results show that the method accounts very accurately for the caffein, especially when the iodine solution is in considerable excess.

In Table No. 2 are given the results obtained where a considerable excess, eight to ten per cent., of sulphuric acid is used. The results are not very uniform and show that slight acidulation gives greater accuracy in the estimation.

The manipulations used by us are as follows: The caffein to be estimated is dissolved in water, acidulated with sulphuric or hydrochloric acid (preferably the latter<sup>1</sup>), avoiding an excess, and made up to a definite volume. The acid strength of this volume should be about one per cent. If the quantity of solution is not large, *i. e.*, not more than forty or fifty cc. the whole is taken; if large an aliquot portion is measured from a burette. Standard Wagner's reagent is run in from a burette, ten cc. at a time, shaking the solution after each addition and allowing it to stand a few moments so that the color of the supernatant liquid may be observed. When this liquid becomes wine-red the iodine solution is in sufficient excess, and the volume of Wagner's reagent added is read, at the same time noting the total volume of the mixed solutions. The caffein periodide is filtered out, after five minutes standing, with a dry asbestos filter, the filtrate collected in a clean dry vessel and transferred to the same clean and dry burette from which the caffein solution first, and later the iodine solution, were measured. (If calibrated burettes are used it is, of course, not necessary to employ the same one each time.)

<sup>1</sup> Caffein solution, 1 to 10000, acidulated by hydrochloric acid, is precipitated by Wagner's reagent, while 1 to 8000 is the limit if sulphuric acid be used.

TABLE NO. I.

Wagner's reagent employed.	I. Solution containing 0.25 per cent. of caffein.			II. Solution containing 0.50 per cent. of caffein.			III. Solution containing 0.75 per cent. of caffein.			IV. Solution containing 1.00 per cent. of caffein.			V. Solution containing 0.50 per cent. of caffein.		
	Taken.	Found.	Per cent. recov- ered.	Taken.	Found.	Per cent. recov- ered.	Taken.	Found.	Per cent. recov- ered.	Taken.	Found.	Per cent. recov- ered.	Taken.	Found.	Per cent. recov- ered.
Theoretical quan- tity plus 2 cc. . .	0.0600	0.0591 0.0589	98.33	0.1200	0.1175 0.1175	97.82	0.1500	0.1481 0.1471	98.40	0.1200	0.1182 0.1179	98.38	0.1200	0.1154 0.1165	96.78
1½ times the theo- retical quantity	0.0750	0.0749 0.0749	99.88	0.1200	0.1191 0.1189	99.17	0.1500	0.1489 0.1485	99.13	0.1200	0.1191 0.1187	99.12	0.1200	0.1196 0.1197	99.75
Twice the theoret- ical quantity.....	0.0500	0.0502 0.0506	100.80	0.0800	0.0805 0.0789	99.63	0.1200	0.1184	98.67	0.1100	0.1091 0.1091	99.18	0.0800	0.0802 0.0791	99.63
One-half of the theoretical quan- tity.....	0.0750	0.0363 0.0363	48.40	0.1600	0.0794 0.0794	49.62	0.2250	0.1107	49.20	0.2000	0.1067 0.1067	53.35	0.1600	0.0791 0.0791	49.44

Columns I, II, III, and IV show the results obtained by decanting the clear liquid after the solutions had stood for one hour. In column V the results are those obtained by filtering the solution for titration through asbestos after five minutes standing.

TABLE NO. 2.

Wagner's reagent employed.	Caffein solution 0.25 per cent.			Caffein solution 0.50 per cent.		
	Taken.	Found.	Per cent. recovered.	Taken.	Found.	Per cent. recovered.
Theoretical quantity + 2 cc.....	0.0500	0.0487 0.0492	97.90	0.0500	0.0468 0.0479	94.70
One and one-third times the theoretical quantity .....	0.0200	0.0204 0.0198	100.50	0.0675	0.0642 0.0639	94.89
Theoretical quantity $\times$ 2.....	0.0250	0.0251 0.0245	99.20	0.0500	0.0480 0.0490	97.00
One-half of the theoretical quantity .....	0.0250	0.0119 0.0128	49.40	0.0600	0.0275 0.0281	46.33

From this an aliquot portion is measured into a porcelain dish and exactly neutralized with tenth-normal sodium thiosulphate. Each cc. of Wagner's reagent consumed = 0.00485 of caffein. The following example will illustrate the method of calculation:

"Unknown" caffein solution 30 cc. + 30 cc. Wagner's reagent = 60 cc.

30 cc. filtrate = 6.2 sodium thiosulphate solution.

Whole solution (60 cc.) containing 30 cc. Wagner's reagent = 12.4 sodium thiosulphate solution.

30 cc. Wagner's reagent—12.4 cc. thiosulphate = 17.6 consumed by caffein.

17.6 cc. Wagner's reagent  $\times$  0.0485 = 0.08536 caffein.

The asbestos filters described are conveniently prepared by placing a small perforated platinum disk in a medium sized carbon tube; on this a layer of glass wool one-fourth of an inch in depth is placed. By aid of a good filter pump, finely divided asbestos pulp, previously acid-washed and suspended in water, is deposited in thin layers by pouring on in small portions and applying suction. This is continued until a layer of asbestos three-fourths to an inch in height is obtained. By keeping the asbestos mixture well stirred during the first part of the operation and allowing it to settle during the latter, the coarser particles will be deposited in the lower layers and the finer ones on the top. The filter is now washed, successively, with hot water, alcohol, and ether, and after drying twenty minutes at 80–100° C., is ready for use.

In the event that it is desired to decant the liquid for titration, instead of filtering, it is advisable to perform the precipitation in

a tall slender cylinder or test-tube on foot. After the precipitate has settled compactly, the end of a burette is immersed in the liquid to the desired depth, and the liquid drawn upward by means of suction produced by a rubber bulb fitted to the top of the burette.

The precaution is always taken, of course, to have the caffein free from any other substance that will affect the iodine solution, and to perform the precipitation in cold solutions.

By the exercise of ordinary care and judgment this method for the estimation of caffein will be found extremely accurate and satisfactory, while with a small amount of practice it admits of very rapid work. Having used it in more than one hundred estimations recently we feel qualified to recommend it.

#### MANIPULATIONS IN THE ASSAY OF KOLA.

*Preparation of Sample.*—Slice a sufficient quantity of the fresh seeds in thin papery slices, allowing them to fall in a beaker of boiling alcohol.<sup>1</sup> An ordinary potato slicer is a very convenient and effective instrument for this purpose. Remove the slices after a few moments' boiling, and allow them to dry spontaneously on clean glass plates. Distil the alcoholic solution, under reduced pressure,<sup>2</sup> to a syrupy consistence, and pour it on the sliced drug now being dried, rinsing the flask with successive small portions of alcohol. When dry remove the drug to a mortar, wash the glass plates with a few cc. of hot alcohol, and pour this on the drug which is to be finely powdered and preserved in dry, glass-stoppered jars. The powder prepared in this way corresponds closely to the original color of the seeds, being but slightly paler in each instance. There can hardly be any doubt that it represents correctly the fresh seeds, with subtraction of the water, and perhaps of a portion of the trifling amount of volatile oil they contain.

*For free Alkaloids.*—Weigh accurately five grams of the sample, transfer to a Soxhlet's extraction tube, and treat for six

<sup>1</sup> The boiling alcohol kills the ferment and also dries the drug quickly. While it will appear later that this ferment, contrary to the general opinion, has but little if any influence on the production of free caffein from the caffein compound, the use of alcohol has nevertheless been retained as an efficient drying agent, and one that preserves the drug apparently without allowing any chemical change whatever to take place.

<sup>2</sup> The object being to avoid the decomposition of the caffein-bearing combination by the hot water remaining after the alcohol is evaporated.

hours, or until exhaustion is complete, with chloroform. Evaporate the chloroform, and to the residue add thirty cc. of hot, one per cent. hydrochloric acid, and filter to remove fat, rinsing out the flask with several small portions of hot water, passing these through the filter, and washing the filter three or four times with hot water. The united filtrate and washings now amount to about seventy to seventy-five cc. Concentrate in a porcelain capsule on a water-bath to about ten or fifteen cc., transfer to a graduated cylinder, which has been carefully compared with the burette to be used for the Wagner's reagent, and rinse the capsule with three or four successive portions of hot water, making up the volume in the cylinder to thirty cc. after cooling. Now run in from the burette thirty cc. standard Wagner's reagent, and agitate well. Filter through asbestos after five minutes, and pour the filtrate into the same burette, previously washed and dried. About fifty-five cc. will be recovered. Run out an aliquot portion of the liquid (say thirty cc.), and neutralize the excess of iodine with decinormal sodium thiosulphate solution, then from the result calculate the number of cc. of iodine solution consumed. Multiply this number by 0.00485 to obtain the weight of the anhydrous caffeine. With another aliquot portion of the filtrate make a duplicate titration.

It will be observed that the alkaloids are estimated only as caffeine. Theobromin also is precipitated by Wagner's reagent but its proportion, 1.48 to 100.00 of total alkaloids, is so small that the error introduced by the difference in the factors of the alkaloids is not appreciable.

*The Combined Alkaloids.*—After the exhaustion with chloroform add alcohol of ninety per cent. to the drug, which is still contained in the extraction tube, and continue the treatment until exhaustion is complete, as shown by the absence of color in the portion of menstruum last siphoned over in the apparatus. Two or three hours are usually sufficient. This alcoholic solution may be treated in either of the following ways :

(a) Evaporate the solution to dryness in a tared porcelain capsule, and weigh. Take a small portion (0.200 or 0.300 gram), and determine the amount of nitrogen by combustion. This nitrogen is entirely alkaloidal, as proteid substances are not



extracted from the drug by the strong alcohol, and the total nitrogen can be calculated into caffein. From the amount of caffein found by combustion of the aliquot portion, calculate the total amount present in the whole extract.

(b) To the hot alcoholic solution add an excess of freshly precipitated lead hydroxide (litharge or lead carbonate will not answer), and digest on a water-bath for a few minutes, until the supernatant liquid is colorless. Then transfer to a porcelain capsule, rinse the flask with hot alcohol, mix with clean white sand, evaporate the mixture to dryness, and place the whole in the extraction tube. Treat with chloroform three or four hours, and determine the caffein volumetrically as previously directed.

We present herewith a table showing the results we have obtained by this plan of assay :

The sample.	Moisture, per cent.	Duplicates.	Fresh kola.			Dried kola.		
			Free alkaloids. Per cent.	Combined alkaloids. Per cent.	Total.	Free alkaloids. Per cent.	Combined alkaloids. Per cent.	Total.
No. 1. Dried kola. (Mixed.)	6.16	I.				1.859	1.783	3.642
		II.				1.828	1.836	3.664
		Av'ge.				1.843	1.809	3.652
No. 2. Fresh kola, red and white seeds.	53.9	I.	0.512	0.927	1.439	Calculated for "dry."		
		II.	0.556	0.841	1.397	1.111	2.011	3.121
		Av'ge.	0.534	0.884	1.418	1.206	1.834	3.040
						1.158	1.922	3.080
No. 3. Fresh kola, red and white seeds, very moldy.	53.9	I.	0.590	0.815	1.405	1.280	1.770	3.050
		II.	0.548	0.893	1.438	1.190	1.938	3.128
		Av'ge.	0.569	0.854	1.423	1.235	1.854	3.089
No. 4. Fresh kola, white seeds.	51.2	I.	0.595	1.029	1.624	1.220	2.110	3.330
		II.	0.562	1.006	1.568	1.153	2.060	3.213
		Av'ge.	0.578	1.018	1.596	1.186	2.085	3.271
No. 5. Fresh kola, red seeds.	57.3	I.	0.503	0.687	1.190	1.180	1.610	2.790
		II.	0.452	0.700	1.152	1.060	1.640	2.700
		Av'ge.	0.478	0.693	1.171	1.120	1.625	2.745

In explanation of the foregoing results, it should be stated that sample No. 1 is not of the same lot of drugs as the other four, but is one that was analyzed in this laboratory last year, and is also African kola obtained then from the house of Frederick Stearns & Co.

In order to facilitate comparison of the fresh and dry drug, the percentages of alkaloids obtained from the fresh have been also calculated for the corresponding amount of dry kola.

These results are much higher than those usually seen, the main difference being that our method accounts for both free and combined alkaloids. It will be seen that about one-half of the total alkaloids of dry kola exist in combination, and in the fresh seeds more than sixty per cent. of the alkaloids are "combined." It should also be noted that so far as the yield of alkaloids is concerned, the moldy kola does not differ from that in perfect preservation. Furthermore there is a difference between the red and the white seeds, as shown by the percentage of alkaloids and moisture.

*Method of Dohme and Engelhardt.*—Dohme and Engelhardt<sup>1</sup> have examined the method employed by Schlotterbeck and Knox<sup>2</sup> and have proposed another one in its stead which has in their hands, given higher results. Their process requires to boil the dried and powdered drug in thirty per cent. alcohol for two hours, filter, evaporate the filtrate to dryness with sand and magnesia and exhaust this residue with chloroform. The residue left after evaporation of the chloroform is dried at 100° C., and weighed as caffein. Using this method they have obtained 2.10 per cent. of caffein from African kola.

We have given their method a careful trial with the gravimetric results stated next below, the sample used being No. 1 of the foregoing table :

- I. 2.04 per cent.
- II. 1.93 " "

*Sources of Error.*—That the caffein thus obtained, although apparently pure, is not so in reality, is shown by the fact that when titrated with Wagner's reagent the per cent. is much lower.

- I. 1.76 per cent.
- II. 1.68 " "

There are still other objections to the method. The treatment with thirty per cent. alcohol does not remove all the free alkaloids, for the drug under assay after having been boiled with the alcohol and washed, as directed, was dried and treated with

<sup>1</sup> *Am. Drugg.*, 1896, p. 12.

<sup>2</sup> *Proc. Am. Pharm. Ass.*, 1895, p. 334.

chloroform in an extraction apparatus. The residue left after evaporation of the chloroform gave positive test for caffein. Nor does the diluted alcohol remove all the combined alkaloids, for after the treatment with chloroform just described, strong alcohol was added to the drug in the extraction tube, and the extraction continued. The wine-red solution obtained was treated with an excess of lead hydroxide, filtered, and the clear colorless solution evaporated to dryness. This residue also contained caffein.

It appears that the combined alkaloids removed by the thirty per cent. alcohol in Dohme's process and treated with magnesia and sand are not completely liberated by this treatment, and consequently are not removed by the chloroform. For after this magnesia-sand residue had been exhausted by chloroform as directed, strong alcohol was used as a menstruum, and it removed another portion of combined caffein, identified by the lead hydroxide treatment above mentioned. In our hands, with careful manipulation, the greatest amount of actual caffein obtained by this method is a little less than one-half of the total amount present, as shown by assay after the process described in this article.

Thanks are due to Mr. Robert J. Nisbet, Ph.C., for valuable assistance rendered in the assays and in the analyses by combustion.

#### GLUCOSIDE OF KOLA.

In the literature of kola is found frequent mention of a glucoside yielding caffein, glucose, and "kola red" on decomposition.<sup>1</sup> It has been stated that this glucoside is an extremely unstable body; that heat, moisture, dilute acids,<sup>2</sup> the ferment<sup>3</sup> of kola, or diastase is sufficient to re-solve it, partly or wholly, into its component parts.

It has even been suggested<sup>4</sup> that no alkaloids exist free in the fresh seeds, but they are wholly combined in this glucoside.

*Methods for Separation.*—The process used by Hilger,<sup>5</sup> and later by Schweitzer<sup>6</sup> for the isolation of this so-called glucoside, "kolanin," is as follows :

<sup>1</sup> R. Knebel, 1892 : *Apoth. Ztg.*, 7, 112.

<sup>2</sup> A. Hilger, 1893 : *Dtsch. Vierteljahres. für Offent. Geshtspfl.*, 25, 599.

<sup>3</sup> C. Schweitzer, 1895 : *Inaugural-Dissertation*, Munich.

<sup>4</sup> Knebel : *Loc. cit.*

<sup>5</sup> *Loc. cit.*

<sup>6</sup> See Schweitzer, 1895 : *Inaugural-Dissertation*, Munich.

The drug is exhausted with alcohol, the extract evaporated to dryness, and the residue washed with water ; then the insoluble portion is dissolved in weak alkali solution. To this, dilute mineral acid is added in slight excess, when the "kolanin" is precipitated. It is collected by filtration, washed with water, and dried. It is a red brown amorphous powder, containing 0.9 per cent. of ash. We have prepared a number of specimens from both the fresh and dried drug, by this process which we shall call Method No. 1. For purposes of comparison we have also employed other processes. In one of these, Method II,<sup>1</sup> the portion of alcoholic extract insoluble in water is dissolved in strong alcohol, and this solution then precipitated by the addition of about three volumes of ether. The precipitate is rapidly filtered at the pump, washed with ether, and dried in a vacuum desiccator over sulphuric acid. The product is a light impalpable powder, cream to light red in color, and is ash-free after three precipitations.

By another method (III) the residue left after washing the alcoholic extract with water was dried in a vacuum desiccator, powdered, and treated with chloroform to remove fat and whatever free alkaloids the water washing had left behind. Again dried and powdered, it furnished a product appearing much like that of Method I, but somewhat lighter colored.

We present herewith (p. 79) a table of results obtained by combustions of samples prepared from both the fresh and the dry seeds by the methods just described.

We do not at present enter upon interpretation of the above results for carbon, hydrogen, and nitrogen,<sup>2</sup> but leave their study until further work on this body, as now planned, shall have been finished. It seems to be largely a question of structure, and this must be settled before it can be positively stated whether the caffein compound in kola is a glucosidal body, or only a glucoside-bearing body. And, of these, the one may not differ from the other except in the order of its stages of decomposition. There is much evidence tending to show that this so-called glu-

<sup>1</sup> In Methods II and III, all distillations are carried on under reduced pressure.

<sup>2</sup> Following are the figures, respectively, of Schweitzer and of Hilger, for the cacao glucoside, the former by calculation from the yield of alkaloids and glucose, the latter by analysis (*Deutsch. Vierteljahr. Oeffentl. Gesundheits.*, 1893, 25, 559.)

GLUCOSIDE OF KOLA.

	Calculated.		Found.											
	By Knebel: <sup>1</sup> $C_{14}H_{12}(OH)_6 +$ $C_6H_{12}O_6 +$ $C_8H_{10}O_2N_4$	By Schweitzer: <sup>2</sup> $C_{40}H_{50}N_4O_{21}$	Method I.				Method II.				Method III.			
			From dry seeds.		From fresh seeds.		From dry seeds.		From fresh seeds.		From dry seeds.		From fresh seeds.	
			I.	II.	I.	II.	I.	II.	I.	II.	I.	II.	I.	II.
Duplicates.														
C .....	52.50	51.71	62.11	61.91	61.82	61.70	61.39	61.71	62.16	61.96	62.06	62.22	61.43	61.26
H .....	6.25	6.03	7.06	7.12	6.98	7.16	6.62	6.79	7.05	7.16	6.80	6.96	6.87	6.98
N .....	8.75	6.03	8.04	7.74	6.04	5.97	5.89	5.67	6.23	5.95	6.92	6.74	6.13	5.94
O .....	32.50	36.23	22.79	23.23	25.16	25.17	26.10	25.83	24.56	24.93	24.22	24.08	25.57	25.82
Caffein by calculation from the N .....	30.31	20.88	27.85	26.81	20.92	20.68	20.40	19.64	21.58	20.61	23.97	23.34	21.23	20.57

<sup>1</sup> Assumed from the proportions of free caffein and glucose found in dry kola.

<sup>2</sup> Assumed from the respective yields of alkaloids and glucose by hydrolysis of the glucoside.

	Cacao glucoside.	
	Calc. by Schweitzer: $C_{66}H_{82}O_{16}N_4$ .	Found by Hilger: $C_{68}H_{84}O_{16}N_4$ .
C .....	65.34	52.85
H .....	7.80	6.22
N .....	5.08	3.63
O .....	21.78	37.30

coside is in reality a mixture of tannates of caffein and theobromin, and that the glucose obtained on hydrolysis is split off from the tannin. These evidences are given a little later on in this paper.

After combustion, the next step was to ascertain, if possible, whether the nitrogen was wholly that of the alkaloids or not.

#### ACTION OF DILUTE ACIDS.

It was attempted to recover the caffein, quantitatively, and for this purpose hydrolysis with dilute mineral acids was first resorted to.

Following carefully the methods of Schweitzer, *viz.*, to boil the "glucoside" for from four to six hours with twenty times its weight of five per cent. sulphuric acid, filter, neutralize the filtrate with barium carbonate, filter again, and estimate the caffein and glucose in the clear filtrate made up to a definite volume, we are unable to obtain results concordant with his. The method was also varied to admit of the removal of the dissolved tannin which remains in the clear filtrate after neutralization with barium carbonate, by precipitating it as lead tannate, filtering, removing excess of lead salt with hydrogen sulphide and boiling off the latter.

The strength of the acid used was varied from two to twenty per cent. and the time of boiling from two to ten hours. But in no case was the amount of caffein recovered equal to that indicated by the nitrogen percentage. In the samples used, the calculated proportion of caffein was, in round numbers, from 21.00 per cent. to 24.00 per cent. Yet 15.00 per cent. was the greatest

amount recovered, and the other amounts varied from that down to 4.76 per cent. the lowest.<sup>1</sup>

Hydrochloric acid diluted to the same strength was next tried with somewhat better but very unsatisfactory results.

It was now in order to institute a control analysis to determine whether or not all the caffein could be recovered after such treatment as has been described. To this end an experiment was made, as follows :

Duplicate samples of 0.300 gram pure caffein, and 0.500 gram pure kola tannin were boiled together with thirty cc. five per cent. sulphuric acid, after which the caffein was estimated in the way above described.

- |     |              |                    |                       |
|-----|--------------|--------------------|-----------------------|
| I.  | Taken 0.300. | Recovered, 0.2635. | Loss, 12.17 per cent. |
| II. | " 0.300.     | " 0.2541.          | " 15.30 "             |

This loss suggested the possibility that some of the caffein might have combined with the tannin. Accordingly the reddish residue filtered out after boiling with acid was dried and exhausted with chloroform to remove all traces of free caffein. Then boiling alcohol was used as a menstruum, and gave a wine-red solution which was treated with lead hydroxide. The clear filtrate on evaporation gave positive evidence of caffein, both by appearance of the crystals and by chemical tests, showing that caffein tannate is actually *formed* during this process of treatment. Now if this is the case, it is hardly to be expected that the so-called "kolanin," a body very similar in properties to caffein tannate, would be quantitatively *decomposed* under exactly the same conditions. Indeed the experiments already described have shown that it is not. Nor is the statement<sup>2</sup> borne out that twenty per cent. sulphuric acid decomposes this natural combination of caffein completely, as the experiment described next below demonstrates.

<sup>1</sup> In this case the extremely low result is to be attributed in part to decomposition of the caffein in the course of the analysis. The tannin dissolved was removed in the way recommended by the United States Department of Agriculture, Division of Chemistry, Bulletin 46, p. 72, *i. e.*, by precipitation with lead acetate, and removal of excess of lead from the filtered liquid by the addition of sodium carbonate. The low result suggested the possibility of the decomposition of caffein by the solution of alkali carbonate, it being well known that alkali hydroxide solutions effect a decomposition into caffeidin, etc., on heating. So an experiment with a known quantity of pure caffein was tried: 0.110 gram caffein was boiled with ten per cent. sodium carbonate solution for four hours; and the caffein estimated volumetrically, 0.0593 gram being recovered, a loss of 46.1 per cent.

<sup>2</sup> Kilmer, 1896: *Am. J. Pharm.*, 96.

1.250 grams of the so-called glucoside were boiled vigorously with forty cc. of twenty per cent. sulphuric acid, and then filtered. The insoluble residue was examined in the way described in the preceding experiment, and "kolanin," apparently unchanged, was found, the evidence being quite positive.

Furthermore, it is not improbable that the hydrolysis of this substance is attended with incomplete recovery of the alkaloid liberated, for the four filtrations necessary, *viz.*, for removal successively of the insoluble red residue, barium sulphate, lead tannate, and lead sulphide are very likely to be accompanied by a loss of caffein from its adhesion to the moist, bulky precipitates.

Hydrolysis with dilute acids having been shown to be unsuited for the purpose of recovering completely the alkaloids from their natural combination, other and entirely different means were resorted to.

#### ACTION OF LEAD HYDROXIDE.

Recalling the fact that this so-called glucoside bears a close resemblance in properties to alkaloidal tannates, and in view of the action of lead hydroxide on this class of bodies, it was decided to try its effect upon "kolanin." Qualitative experiments to this end proving successful, it was next in order to ascertain whether or not the liberation of caffein was quantitative, and a full recovery possible. For this purpose 0.500 gram of the so-called "kolanin," whose average nitrogen content indicated 0.1052 gram caffein, was dissolved in twenty-five cc. hot ninety per cent. alcohol. To this, freshly precipitated lead hydroxide previously triturated with hot alcohol to a smooth cream was added, until, after a few moments' standing to allow subsidence of the precipitate, the liquid was clear and colorless. The mixture was then evaporated to dryness on a water bath, clean dry sand added to give the requisite volume, the whole then transferred to a Soxhlet's tube, and the beaker carefully rinsed with chloroform, the rinsings being added to the contents of the tube. Chloroform was then added, and extraction continued for two hours. The chloroform solution was then evaporated, and the caffein estimated volumetrically, 0.1040 gram being recovered.

This treatment does not decompose caffein, for 0.200 gram pure caffein dissolved in alcohol with 0.500 gram pure kola-



tannin and treated as above described yielded 0.1991 gram on volumetric estimation.

This simple and rapid process for liberating the caffein from the caffein compound affords a means for a very accurate determination of the combined alkaloids of kola, of which fact use has been made in the method of assay proposed and used by us, as previously described.

This reaction of kolanin with lead hydroxide indicates a tannate-like character for the body. There is reason to think that the glucose obtained by decomposing this so-called glucoside with mineral acids exists primarily in combination with the tannin-like body, for after chloroform had removed all the caffein from the mixture of alkaloids, lead salt, lead hydroxide and sand, described above in the experiments with "kolanin," treatment with water removed nothing further. The liberation of glucose therefore is not necessarily simultaneous with that of caffein, nor in consequence of it. This was further shown by decomposing the lead salt formed by the red coloring matter, through treatment with hydrogen sulphide, and thereby recovering the colored body previously combined with the caffein. This body so obtained, gives all tannin reactions toward iron salts, alkaloids, gelatin, etc., and has a pronounced astringent taste. On treating it with dilute mineral acid, in the manner directed by text-books,<sup>1</sup> very positive evidence of glucose was given, not only by its behavior with Fehling's solution, but with phenylhydrazin as well, of which mention is made later. The foregoing facts would seem to indicate that the so-called glucoside is a combination of caffein (and theobromin) with a glucoside tannin.

#### ARTIFICIAL KOLA-TANNATE OF CAFFEIN. METHOD OF PREPARATION.

By way of further investigation into this question we undertook to prepare artificially from kola-tannin and pure caffein a similar product which we proposed to compare with the natural compound. This was successfully accomplished as follows: An aqueous infusion of kola is poured into a ten per cent. solution of caffein acidulated with hydrochloric acid. The presence of

<sup>1</sup> Prescott: Organic Analysis, 467.

acid is necessary to obtain an aqueous caffein solution of sufficient concentration, and especially to avoid the re-solution of the tannate of caffein which takes place in the neutral solutions in the presence of an excess of either tannin or caffein. The precipitate, abundantly formed, is rapidly filtered at the pump, washed with cold water, and well drained. It is then dissolved in alcohol, and filtered to remove insoluble extraneous matter carried down in precipitation. The alcohol is then distilled off under reduced pressure until the solution has reached a syrupy consistence, and the evaporation continued to dryness over sulphuric acid in a vacuum desiccator.

PROPERTIES OF KOLANIN AND CAFFEIN KOLA-TANNATE COMPARED.

The product obtained is identical in appearance and sensible properties with the so-called kolanin. Both are insoluble in water, ether, chloroform, and cold dilute mineral acids; freely soluble in alcohol with dark wine color, from which solution they are re-precipitated by two or three volumes of ether; soluble in dilute acetic acid, more easily on warming; sparingly soluble in warm acetone; soluble in warm neutral caffein solution, and in warm kola-tannin solution; quite soluble in dilute alkali (both fixed and volatile) solution<sup>1</sup> with production of a very dark color, and at once reprecipitated therefrom by dilute mineral acids in slight excess, also by acetic acid, though the precipitate redissolves in an excess of the acetic acid on warming. They are decomposed in alcoholic solution by lead acetate and lead hydroxide. In all the ways tried both deport themselves alike and in a manner not inconsistent with the chemical behavior of an alkaloidal tannate.

Pure kola-tannin was also used for the preparation of the caffein salt, and yields a product identical in appearance and properties with that prepared from the impure kola-tannin of aqueous infusion of kola. But as the compound of the pure tannin does not apparently differ from the precipitate of caffein with kola infusion, the latter, less difficult of preparation, has been em-

<sup>1</sup> Considerable caffein may be removed from this alkaline solution by shaking out with chloroform. It is possible that the tannate is decomposed in part or wholly by the alkali and reformed upon addition of acid. The process is wasteful, so it is likely that the re-formation, if it occurs in this way, is complete.

ployed in the preparation of the several samples of caffein kola-tannate used for determining elementary composition, namely :

I. Prepared as described above. Reddish-brown powder, with astringent and bitterish taste.

II. In same way as Number I, the final product being dissolved in dilute alkali solution, and reprecipitated by dilute hydrochloric acid, filtered, washed, and dried. Reddish-brown powder, with astringent and bitterish taste.

III. In the same way as Number I, except that the final product was dissolved in alcohol and precipitated by ether, filtered, washed with ether, and dried. Lighter in color, but similar in taste to Number I.

IV. The clear filtrate after the precipitation of Number I gave, on twenty-four hours' standing, another copious precipitation of caffein kola-tannate, which was recovered in the usual way. Appearance and taste like that of Number I.

The following table shows the results obtained by duplicate combustion of each of these samples for carbon, hydrogen, and nitrogen :

CAFFEIN KOLA-TANNATE—ARTIFICIAL.

Found.

Method.	I.		II.		III.		IV.	
Duplicates.	1.	2.	1.	2.	1.	2.	1.	2.
C .....	59.27	59.41	60.11	59.89	59.64	59.35	59.94	60.22
H .....	6.21	6.02	6.18	6.07	5.96	6.10	6.08	6.24
N .....	6.20	5.96	5.30	5.54	5.61	5.45	5.15	5.27
O .....	28.32	28.61	28.41	28.50	28.79	29.10	28.83	28.27
Caffein calculated from the N .....	21.47	20.64	18.35	19.19	19.43	18.87	17.83	18.25

It will be seen by comparing these figures with those given for the natural form of combined caffein extracted from kola by physical solvents in our method, that the composition of the one does not differ very widely from that of the other, and that this artificial product has a fairly uniform and constant composition. It is, of course, a well-understood fact that the composition of alkaloidal tannates is by no means strictly constant, but that it varies according to temperature and concentration of solutions

used, and the mass of each used with respect to that of the other. The well-known variation in the composition of the same kind of tannin, obtained under different conditions, is also to be taken into account. The natural form of combined caffein, called kolanin, yields on an average about twenty-two per cent. of caffein, while that obtained artificially gives a slightly lower amount, about nineteen per cent. being the average. The difference may, perhaps, be due to the different conditions of formation, and not to any difference in the character of the bodies themselves. And, as previously stated, so far as reactions and physical properties are concerned, leaving a slight difference in elementary composition out of consideration, we have not thus far found any radical difference between the natural and the artificial products.

#### ACTION OF FERMENTS.

In order to ascertain whether or not diastase would liberate caffein from the so-called glucoside, the following test was made: 0.500 gram of the natural caffein compound of kola, and 0.0500 gram of pure diastase,<sup>1</sup> known to be 1 : 100, in twenty-five cc. distilled water, were kept at a temperature of 50°–53° for twenty-four hours, and for thirty-six hours at the ordinary temperature; the caffein liberated was then estimated. A control test was made at the same time, using the same amount of the caffein-bearing body, and the same volume of water, but no diastase. This was kept under exactly the same conditions of temperature and time as the first, and the caffein then estimated.

Sample with diastase yielded 0.0689 caffein, equal to 56.50 per cent. of the whole amount present.

Sample without diastase yielded 0.0706 caffein, corresponding to 58.83 per cent. of the total amount present.

This experiment was repeated on the artificial caffein kola-tannate with similar results.

These results indicate that the liberation of caffein is not due to the diastase, but to the water and heat used for its exhibition.

It was next in order to learn, if possible, the influence of the ferment of kola on the liberation of caffein from its combination

<sup>1</sup> Prepared by Mr. D. L. Davoll, Jr., Instructor in Organic Chemistry in the School of Pharmacy of this University, to whom our thanks are due.

existing in kola. For this purpose several perfectly fresh and sound red and white seeds were selected. One-half of the number were sliced into sixty cc. of water and kept for sixteen hours at 50°–55° and for twenty-four hours at ordinary temperature, then evaporated to dryness, powdered, and the free caffein estimated in duplicates in a weighed portion. The other half of the seeds were similarly treated, except that the slices were received in boiling water to destroy the ferment; and the whole was then kept at 50°–55°, the same length of time as those described above, then evaporated to dryness, powdered, and assayed.

Sample.	Per cent. Caffein. <sup>1</sup>	
	I.	II.
Not sterilized .....	0.644	0.639
Sterilized .....	0.629	0.662

It would seem from the above stated results that the kola ferment does not assist in the liberation of caffein from its natural combination, but that such liberation as takes place is rather to be attributed to the presence of moisture and warmth.

Moreover, it is of significance respecting the caffein compound, to observe that sterilizing the kola, which checks the formation of the colored body called kola-red, does not at the same time check the liberation of the alkaloid. In other words, it does not at all appear that caffein and kola-red are joint products of the one hydrolysis of a glucoside, though such has been the conclusion of previous investigators.

#### ESTIMATION OF THEOBROMIN.

This alkaloid forms such a small proportion of the total alkaloids that it is usually ignored in an assay, the whole being computed as caffein. As its ratio to the caffein present seems to be pretty constant, there appears no particular objection to this procedure unless a very precise analysis is desired.

We have found the gravimetric method proposed by Kunze,<sup>2</sup> with a few modifications, very satisfactory for the estimation of theobromin in the presence of caffein.

<sup>1</sup> Calculated for fresh seeds.

<sup>2</sup> W. E. Kunze, 1894: *Ztschr. anal. Chem.*, 24.

It is, however, necessary to purify the alkaloids by recrystallizing twice from water, or the traces of tannin and coloring matter adhering will reduce the silver nitrate and lead to erroneous results. After purification and drying at  $100^{\circ}$  C., 0.500 gram of the alkaloids of kola is dissolved in twenty-five cc. water, a few drops of ammonia added, and then five cc. silver nitrate solution (reagent), and the liquid heated on a water bath until the ammonia is entirely expelled. The silver theobromin is precipitated, and collected on a weighed asbestos filter, and washed with hot water until the washings no longer show the presence of a silver salt by the addition of hydrochloric acid. Hot dilute hydrochloric acid is now passed through the filter, followed by hot water until the washings are free from all traces of hydrochloric acid. The silver chloride remaining in the filter is now washed successively with alcohol and ether, dried twenty minutes at  $85^{\circ}$ – $100^{\circ}$  C. and the tube weighed. From the weight of the silver chloride we have the proportion:

Molecular weight of AgCl : Molecular weight of  $C_7H_8N_4O_2$  :: Weight of AgCl :  $x$  = weight of the theobromin.

In total free alkaloids the proportion of theobromin was found to be 1.48 per cent., and in the total combined alkaloids, as would be expected, very nearly the same, in this case 1.51 per cent. Schweitzer,<sup>1</sup> however, found that it constituted 19.70 per cent. of the total combined alkaloids, and suggested that the increased amount of theobromin may be due to its formation from caffein by the prolonged boiling with the five per cent. sulphuric acid used by him for hydrolysis of the supposed glucoside.

But as a matter of fact, a methyl group is not so easily eliminated from caffein. That five per cent. sulphuric acid will not effect this change is shown by the results of the experiment next described. 0.3494 gram of caffein boiled for six hours with twenty-five cc. of five per cent. sulphuric acid showed at the end of that time not the slightest trace of theobromin by the silver nitrate test previously mentioned, and 0.3485 gram was recovered. Nor is caffein changed or colored by concentrated sulphuric acid even at  $100^{\circ}$  C.<sup>2</sup>

<sup>1</sup> 1895: Inaugural Dissertation, University Munich.

<sup>2</sup> Prescott's Organic Analysis, p. 82; Allen's Commercial Organic Analysis, vol. iii, pt. ii, 474.

Schmidt<sup>1</sup> found that by heating caffein with concentrated hydrochloric acid in a sealed tube for six to twelve hours, at 250° C., ammonia, sarcosin, methylamine, carbon dioxide, and traces of formic acid were formed, but no theobromin; he also found that concentrated hydrochloric acid has no action on caffein below 200°.

#### MELTING-POINT OF THE ALKALOIDS.

After repeated purification, the melting-point of the mixed free alkaloids of kola was taken, as was also that of the combined alkaloids; both were the same, 225°–227°, corresponding fairly well with that of pure caffein.

#### TANNIN.

(1) *Free Tannin*.—This was separated in various ways, the preferred method being as follows, taken in part from Allen:<sup>2</sup> The drug is exhausted with ninety-five per cent. alcohol, the alcoholic solution distilled *in vacuo* to a syrupy consistence, then washed with cold water. The insoluble matter is removed by decantation or filtration, and the clear wine-red solution fractionally precipitated with lead acetate (or lead hydroxide), the first and last portions of lead tannate being rejected. The lead tannate after being well washed is suspended in alcohol and decomposed with hydrogen sulphide. After filtration the alcoholic solution of tannin is distilled *in vacuo* to syrupy consistence and evaporation finished in a vacuum desiccator over sulphuric acid.

The tannin thus obtained is light-red to red-brown, having a faintly acidulous and decidedly astringent taste; deports itself as other tannins do towards iron salts ("iron greening"), gelatin, alkaloids, etc., etc. It is a glucosidal body, yielding on hydrolysis with mineral acids a dark-brown body. This was found to be insoluble in water or alcohol, and to give, on combustion, 69.20 per cent. of carbon, and 6.70 per cent. of hydrogen;<sup>3</sup> with the dark brown body was obtained glucose, identified by its action on Fehling's solution, and towards phenylhydrazin, with which latter it forms an osazone. We did not

<sup>1</sup> E. Schmidt: *Ann. Chem.* (Liebig), 217, 270.

<sup>2</sup> Allen's *Commercial Organic Analysis*, vol. iii, pt. i, p. 76.

<sup>3</sup> These figures do not correspond with those given by Knebel for kola red  $C_{14}H_{12}(OH)_6$ .

obtain a sufficient quantity of this osazone to take its melting-point, but its presence gave evidence of the glucosidal nature of the tannin.

(2) *Combined Tannin*.—The tannin existing in kola in combination with the caffein (as the so-called glucoside) was separated by means of lead hydroxide, following the above described manipulations. This "combined" tannin agrees in appearance and properties with the free tannin already described, being also a glucoside tannin.

The results obtained by combustion are also stated next below:

Duplicates.	Free tannin.		Combined tannin.	
	I.	II.	I.	II.
C.....	53.36	53.57	55.61	55.78
H.....	5.19	5.28	5.37	5.54
O.....	41.45	41.15	39.02	38.68

All calculations upon the composition of this body are reserved until after further work in its separation.

ANN ARBOR, MICH., JULY 6, 1896.

## OBITUARY.

DR. HENRY A. MOTT, who has been an active member of the American Chemical Society since its organization in 1875, died at his home in New York City, on November 8, 1896. He was a grandson of the famous surgeon Dr. Valentine Mott, and was born at Clifton, Staten Island, New York, October 22, 1852. His primary education was obtained in the private schools of Rev. Mr. Tufts, at Munson, Mass., and of Prof. Berthet, on Broadway, near 18th street, in New York City. Later he entered the Academic Department of Columbia College, but finding the courses of study therein not wholly suited to his tastes and ambition, he applied for work leading to the degree of Doctor of Philosophy. On June 14, 1869, he entered the School of Mines in the course of mining engineering, and in 1873 he was graduated, receiving at the same time the degree of Bachelor of



Philosophy in metallurgy and Engineer of Mines in the course of engineering.

In pursuance of his studies in the School of Mines, he showed special aptitude for chemical work, and after his graduation, during the months of August and September, 1873, he served as private assistant to Dr. Charles F. Chandler in the laboratory of the School of Mines. In 1874 he was appointed chemist to the sugar refining firm of Havemeyer & Elder, in which capacity he served for seven years, or until 1881. While connected with the sugar refinery, and during 1875 and 1876, he was enrolled as a post-graduate student in Columbia College, and in the summer of the latter year, in consequence of the work prosecuted in this connection, he was awarded the degree of Doctor of Philosophy.

In 1881 he was elected Professor of Chemistry in the New York Medical College and Hospital for Women, and he continued in this professorship during five years. About this time he became identified with the manufacture of oleomargarine and artificial butter by the method of Megé-Mouries, and devised a process for preventing the crystallization of the product, so prejudicial to its commercial value.

His work now became directed to the study of foods and their adulteration and his activity in this particular led to his appointment to the office of Food Inspector of the Bureau of Indian Affairs under the United States Department of the Interior, in which he was called upon to make chemical examination of all food materials supplied by the government to the Indians.

His efforts were later directed to toxicological investigations and he was elected chemist to the New York Medico-Legal Society, to which he contributed many papers relating to the action of poisons in the animal system, their distribution in the cadaver and their detection in animal matter.

Among the well-known cases in which his services were engaged are the Belmont horses cases, in which the animals were poisoned with silver nitrate and corrosive sublimate, respectively; the celebrated Ben Ali or Shakespeare case, in which he was retained by the French Government for the defense; and the Fleming case, lately tried in New York City.

At the time of his death he was one of the lecturers in the

Free Lecture Course organized under the direction of the Board of Education of New York City, and he served actively in this connection during the six years immediately preceding his death. Among the subjects treated by him in course are, "Fire and the Methods of Extinguishing," "Light and Color," and "The Five Senses."

The more important of his chemical work is represented in the following titles from among his published books and papers:

"Milk of the African and Caucasian Races," 1876; "Artificial Butter," 1876; "The Scientific Manual," 1876; "The Chemist's Manual," 1877; revised in 1882; "The Adulteration of Milk," 1878; "Examination of Quinine," 1879; "Absorption of Sugar," 1879; "Alumina Salts on the Gastric Juice," 1879; "Alum Baking Powders," 1880; "The Megé Discovery—Oleomargarine Butter," 1880; "Oleomargarine and Oleomargarine Butter," 1880; "Memoirs on Oxygen," 1881; "Post-Mortem Imbibition of Poison," 1889; "Expert Testimony."

In 1886 the University of Florida conferred upon him the degree of Doctor of Laws.

In addition to his other literary work he published a book entitled "Yachts and Yachtsmen of America," and another discussing the question, "Was Man Created?"

Dr. Mott was most enthusiastic in the prosecution of any enterprise or investigation in which he became interested and his industry is shown in his published results. He was a genial companion and a faithful friend, and he will be missed from among the circle of his associates even as he is from his home. In his death the Society loses one of its useful members.

WM. McMURTRIE.

## BOOKS RECEIVED.

Chemistry for Engineers and Manufacturers. By Bertram Blount and A. G. Bloxam. Volume II. Chemistry of Manufacturing Processes. With illustrations. 484 pp. Philadelphia: J. B. Lippincott Co. London: Charles Griffin & Co., Ltd. 1896. Price \$2.50.

Bulletin No. 44. Second Series. Charbon or Anthrax, with experiences during recent outbreak in North Louisiana. By S. B. Staples and W. H. Dalrymple. Baton Rouge: Louisiana State Experiment Station. 52 pp.

# THE JOURNAL

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## AMERICAN CHEMICAL SOCIETY.

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### SOME PRESENT POSSIBILITIES IN THE ANALYSIS OF IRON AND STEEL.<sup>1</sup>

BY C. B. DUDLEY.

To the analytical chemist, there are few substances in nature, more interesting than a piece of pig iron, few substances which have received more study, and few which present chemical problems more difficult of solution. The amount of work which has already been done in connection with this very common but very complex substance, is something enormous. Indeed, if we add to the study which has already been put on pig iron itself, the work which has been done on what may perhaps fairly be called its progenitors, *viz.*, the ores, the fuel, the flux, and the refractory materials used in its production, and then consider still farther the labor already expended in the analysis of what we may call the progeny of pig iron, *viz.*, castings, wrought iron, malleable iron, and the numerous grades and kinds of steel, made by the various processes of the present day, we shall surely be safe in saying that more chemical work has been done in connection with pig iron, than with any other substance in nature. Is it too much to affirm that at the present time one-third, possibly one-half of all the chemical work done in the world, is in connection with the iron industry, either in the solution of unworked-out problems, the development of new methods of analysis, or in the routine analyses affecting the interests of producer and consumer.

But the amount of work already done and in daily progress in connection with this substance, is not all that may be said in

<sup>1</sup> Presidential address delivered at the Troy meeting of the American Chemical Society, December 29, 1896.

regard to it. The complexity of pig iron is very great, and consequently the analytical problems presented are far from being easy of solution. It may not be uninteresting to enumerate some of the substances which have already been found in pig iron. We find, besides the element iron, carbon, phosphorus, silicon, sulphur, manganese, copper, chromium, tungsten, titanium, vanadium, nickel, cobalt, aluminum, potassium, sodium, magnesium, calcium, and lithium. It is fair to say that there is apparently well grounded belief that the last five are characteristic of intermingled slag, rather than of the metal itself. It is not intended that it should be understood that all of these substances have been found in any one sample of pig iron, but that all these substances have actually been detected in the analysis of this alloy. Indeed there seems no reason why any element, which either occurs in the metallic condition in nature, or which is reducible to that condition by carbon, and which is not volatile at the temperature of the blast furnace, may not occur in pig iron, provided of course it will alloy with the metal. Quite a large number of other substances besides those mentioned above have actually been alloyed with some form of iron or steel. Among these may be mentioned zinc, tin, lead, antimony, bismuth, molybdenum, silver, platinum, rhodium, iridium, palladium, and gold. Nor is this all that may confront the analyst, who devotes himself to the chemistry of iron and steel. Not less than three elements which usually exist in nature in the gaseous form, occur in these metals, and are believed to have important influences on their physical properties. These are oxygen, hydrogen, and nitrogen; while the numerous analyses show the presence of carbon monoxide in both cast iron, wrought iron, and steel. It seems quite evident that the chemist who hopes to successfully cope with the problems which are involved in even the ultimate analysis of iron and steel in their various forms, must be well equipped with a liberal share of the methods and processes known to mineral chemistry, and on the other hand, if he attempt the proximate analysis of these substances, or the separation and determination of the various compounds of the elements present, with iron or with each other, he will at least be brought on the border ground of organic chemistry. Some of the carbon compounds

which are characteristic of the brilliant work of the present president of the French Chemical Society, are known to occur in or have already been isolated from pig iron.

It would lead us too far from our present purpose to do anything more than enumerate the largest number of the elements given above. Suffice it is to say that in what follows, we shall confine ourselves to the five first mentioned; *viz.*, carbon, phosphorus, silicon, sulphur, and manganese. And the question which we shall ask ourselves is, 'What is the present condition of a portion of the analytical methods for the determination of these substances, considering these methods both in regard to their accuracy and speed?' One word of precaution. It would be manifestly impossible to comment on all the methods in use for determining these constituents. To enumerate them alone would weary your patience. We shall confine ourselves, therefore, principally to methods which may be or are used when the diverse interests of producer and consumer are involved.

Beginning then with total carbon in pig iron, wrought iron, and steel, we deem it safe to say that the method by combustion in oxygen gas, as at present known and worked in many laboratories, leaves very little to be desired, so far as accuracy is concerned, and is sufficiently rapid for most commercial uses. The modification introduced some years ago, of using a solution of the double chloride of copper and ammonium, instead of simple chloride of copper,<sup>1</sup> to release the carbon from the iron, took away from the combustion method, one of its greatest difficulties; *viz.*, the long time required to dissolve the metal. This modification, as many will doubtless remember, reduced the time required for solution, from two or three days, to an hour or less. Indeed, at the present time, if a good stirring machine is used, it is quite possible to dissolve three grams of fairly fine borings of pig iron, wrought iron, or steel, in 200 cc. of the proper solvent in from ten to forty minutes. Still further the studies of the Committee on International Standards for the

<sup>1</sup> It is difficult to say positively who first suggested this modification. The first mention in literature that we are able to find is in the *Transactions of the American Institute of Mining Engineers*, 4, 157, by J. B. Pearse. But a private communication from Andrew S. McCreath, states that he made the suggestion while working under Pearse, and that Professor Richter, in the *Leoben Jahrbuch*, had previously suggested the use of potassium or sodium chloride with copper chloride, which led him to try the ammonium salt. McCreath's description of the method as used by himself, is published in the *Transactions of the American Institute of Mining Engineers*, 5, 575.

Analysis of Iron and Steel, have further modified the method, and it is believed rendered it much more accurate. Among these modifications may be mentioned the use of an acid instead of a neutral or basic solution of the double salt to dissolve the metal. This point was thoroughly worked out by Blair.<sup>1</sup> Following this came the work done in the laboratory of the Pennsylvania Railroad Company,<sup>2</sup> demonstrating the unreliability of the use of the double chloride of copper and ammonium as a solvent, owing, as appeared later, to the probable presence in all ammonia and its salts, obtainable in the market, even those marked "C. P.," of some carbonaceous material, possibly pyridine,<sup>3</sup> derived from the gas liquor used in making the ammonia. The substitution of the potassium,<sup>2</sup> for the ammonium salt, has apparently completely overcome this difficulty, and this with the use of oxygen gas instead of lead chromate, in which to burn the carbon, and some modifications of the absorbing and purifying train,<sup>3</sup> have seemingly placed the dry combustion method for determining carbon in the front rank of successful and accurate analytical processes. The principal known source of error in the method at the present time appears to be in connection with the weighing. The potash bulbs and small calcium chloride tube used in absorbing the carbon dioxide weigh, altogether, some fifty to sixty grams, and present considerable surface. If now, between the weighing before the combustion and the weighing after the combustion, the interval being an hour, or a little more, there is considerable change in the hygroscopic condition of the atmosphere, an error of 0.01 percent. may be easily introduced. If we may trust our experience, it is difficult to make closely agreeing duplicate combustions in showery weather. Blair suggests a method of overcoming this difficulty consisting in having a second potash bulb and calcium chloride tube of, as nearly as possible, the same size on the opposite end of the balance when weighing.

In regard to the accuracy of the method as at present understood, it may be said, that undoubtedly the best test of the accuracy of a method, is the recovery of a known amount of any substance added to the material to be analyzed. This proce-

<sup>1</sup> *Trans. Am. Inst. Mining Eng.*, 19, 614.

<sup>2</sup> *Trans. Am. Inst. Mining Eng.*, 20, 242.

<sup>3</sup> *This Journal*, 15, 448.

ture being manifestly impossible in the case of iron and steel, we are compelled to judge of the accuracy of the combustion method, as applied to these metals, in some other way. For this purpose, however, we have at hand the results obtained by different chemists, using different methods, but working on the same samples. In the course of the work done by the Committee on International Standards for the Analysis of Iron and Steel, the carbon in four samples of steel was determined, First, by using acid double chloride of copper and potassium as solvent and burning in oxygen gas; Second, by using the same solvent and burning in chromic acid solution; and Third, by treating the borings direct with bisulphate of potash and heat, conducting the carbon monoxide and sulphur dioxide formed over hot solid chromic acid, which oxidized both gases and retained the sulphur trioxide formed, and finally measuring the volumes of the resulting carbon dioxide in an eudiometer tube. Each method was used by a different chemist. The results obtained are as follows, the letters at the side representing the four samples of steel, the figures at the top representing the chemists, and the figures in the columns the percentages of carbon in the steel samples :

	1.	2.	3.
A.....	1.455 <sup>1</sup>	1.440 <sup>1</sup>	1.450 <sup>2</sup>
B.....	0.815	0.800	0.815
C.....	0.450	0.450	0.448
D.....	0.152	0.185	0.168

The agreement of the results on the first three samples is quite marked. The discrepancy on the fourth sample has not been explained. The matter is discussed in considerable detail in reference 1, but we think it safe to conclude that so far as method goes, the determination of total carbon in pig or cast iron, wrought iron and steel, is reasonably accurate.

The speed of the combustion method as at present worked in good laboratories is quite remarkable, compared with the possibilities twenty-five years ago. A sufficient supply of sample borings being at hand, one operator using two furnaces, may readily make from fourteen to sixteen combustions in a day of eight hours, it being understood that the bulbs are weighed with

<sup>1</sup> *Proc. Eng. of Western Penna.*, 9, [9], 35.

<sup>2</sup> *Ztschr. anorg. Chem.*, 4, [3] und [4], 505.



oxygen gas in them instead of air, and that the last weight of each combustion, except the last one at night, is taken as the first weight of the succeeding one. It is, of course, assumed that when turning out the amount of work above described, the furnaces and apparatus are all in good order, and everything working well. Accidents, an occasional overhauling of the apparatus, blank combustions from time to time for testing purposes, and once in a while an obstinate steel that refuses to dissolve in time or gives trouble in filtration, will all tend to diminish output. The results obtained with this rapid work show, when duplicates are made, occasional discrepancies as high as three hundredths of a per cent. in a steel containing one per cent. of carbon, but we have seen very large numbers of duplicates, made as above described, which did not disagree one one-hundredth.

Again, when work is not so plentiful as to admit of the procedure described above, the method still permits satisfactory speed. Starting with a fresh sample of borings and everything in good order, but cold, it is not difficult to get two closely agreeing determinations on the same sample in two hours and a half. Of course, in investigation or referee work, more time would undoubtedly be used, especially if the interests involved are very great. But we have many times been astonished in our own laboratory, at the close agreement between the results obtained in the rapid manner described above, and the duplicate analysis made on the same sample for confirmatory purposes, but using much more time and pains.

Turning now to the determination of combined carbon and graphite, we do not find the state of affairs so satisfactory. As is well known, these two constituents are usually found by first determining total carbon, then dissolving another portion of the sample in hydrochloric acid, filtering and washing with caustic potash, alcohol, and ether, and then burning the residue, collecting and weighing the carbon dioxide formed, as in an ordinary combustion. The result is called graphite, and the combined carbon is the difference between the total carbon, and the graphite. But as Shimer<sup>1</sup> has so well shown, what we actually get by this procedure is not necessarily the graphite and the

<sup>1</sup> *Trans. Am. Inst. Min. Eng.*, 25, 395.



total combined carbon in the sample, but only the combined carbon which exists in the metal as a carbide soluble in hydrochloric acid. If the sample contains carbides not soluble in that acid, nor in the materials used in washing, the carbon of these carbides appears with and is counted as graphite. Shimer shows that titanium, and possibly vanadium carbide, are apparently not infrequently thus counted. The use of sulphuric instead of hydrochloric acid leads to the same error, while the employment of nitric acid as solvent, apparently gives the graphite much more definitely, but leaves us in doubt as to whether the combined carbon is really the combined carbon which we want, in order to have light on the quality of the metal we are dealing with. It is obvious that the difficulty here is in our lack of knowledge as to what carbides actually exist in pig and cast iron, and if there are several of them, which one or ones do we actually want to know the carbon content of. If we knew positively that the combined carbon wanted was that which exists in the metal as carbides of iron and manganese, and that these carbides were soluble in hydrochloric or sulphuric acid, while all other carbides present were not soluble in these acids, obviously we should use these acids when determining combined carbon. On the other hand, if we want to know only graphite, and care little about the combined carbon, apparently nitric acid is the solvent to use. It is clear that much more work is needed on this subject, a state of affairs which as we progress, we shall find is characteristic of other constituents of the metals we are considering.

Much might be said in regard to the color test for determining carbon in steel. It is difficult to over-estimate the value and importance of this method, especially in the daily operation of steel works, and there seems little doubt but that if proper precautions are employed, the method in skillful hands will give results that are fairly reliable to within three or four-hundredths of a per cent. It would hardly be possible in this paper to discuss all the precautions which are deemed essential by those best informed. A chemist of wide experience with the method, has enumerated twenty-four points that must be observed, if reliable results are to be expected. Let it suffice for us to say that even approximate accuracy cannot be expected.

1. If the steel whose carbon is to be determined and the standard steel do not have their carbon in the same condition. For example, if the standard steel has been annealed, and the sample to be tested has been tempered, the results will be worthless.

2. If the attempt is made to determine the carbon in any steel by using a standard widely different from it, in carbon content. Using a 0.20 per cent. carbon standard, with a steel containing 0.50 or 0.60 per cent., is apt to lead to very fallacious results.

The best results seem to be obtained by having the carbon in all steels both standards and tests in the condition given by annealing, by having a number of standards which differ little from each other in carbon content, and by not attempting to use the method on steels containing very little or very large amounts of carbon. It may not be amiss to add here that the practice so prevalent in many of the steel works, of using this method for all carbon determinations, including those where contracts are involved, is reprehensible and should be discontinued. The chemist at the works does the best he can with the method he is using, and the amount of work required of him, as well as the facilities furnished, do not admit of the use of a better method. On the other hand when a dispute arises, and it is ultimately shown that the works are in error, the chemist is blamed and analytical chemistry brought into disrepute, not because either is really at fault, but because more is expected of the color test method, than it is really able to give. To the steel makers we say, "Do not expect your chemist to render you the bricks of good chemical analyses, without you give him the requisite straw of time and appliances to do good chemical work."

Few of the constituents of iron and steel have more important influences on their valuable qualities than phosphorus, and upon few has more chemical work been done. The present condition of the methods for determining this constituent, seems fairly satisfactory provided we are willing to take time enough to do the work. In confirmation of this statement, the work<sup>1</sup> done by the Sub-committee on Methods of the International Committee on Standards for the Analysis of Iron and Steel may be cited. This sub-committee consisted of five members, each of whom analyzed five samples of steel, and each used his own method, without any

<sup>1</sup> *Proc. Am. Soc. Civil Eng.*, 21, 59.

attempt at consultation or agreement with each other before the work was done. The methods employed may be briefly indicated as follows, those interested being referred to the report of the committee published as per the reference given for the details. Mr. Blair used what is known as the acetate method. Mr. Shimer used the molybdate magnesia method. Your speaker used a combination of the acetate and molybdate magnesia methods. Dr. Drown used a combination of certain features of the modern rapid methods with the molybdate magnesia method. And Mr. Barba on one sample used the acetate method as described by Blair, and on the other four samples employed certain features of the molybdate method to separate the phosphorus from the iron, and then used the reductor to get the amount of phosphorus, instead of weighing as magnesium pyrophosphate. It will be evident to any one carefully reading the report referred to, that the methods employed differed widely in principle, in strength of solutions, and in manipulation, and yet these methods gave the following percentages of phosphorus in the five samples :

	1.	2.	3.	4.	5.
Mr. W. P. Barba.....	0.041	0.015	0.095	0.091	0.041
Mr. A. A. Blair .....	0.040	0.016	0.098	0.091	0.041
Dr. T. M. Drown ....	0.042	0.016	0.104	0.090	0.042
Dr. C. B. Dudley . . .	0.040	0.016	0.099	0.097	0.039
Mr. P. W. Shimer.....	0.041	0.017	0.098	0.096	0.039

In explanation of the results, we quote from the report of the sub-committee.

"Sample No. 1 is an ordinary open-hearth steel. Sample No. 2 is a crucible steel. Sample No. 3 is an open-hearth steel to which metallic arsenic was added while in the molten condition in a crucible. Sample No. 4 is an ordinary Bessemer rail steel. Sample No. 5 is the No. 5 sample of the Committee on International Standards, and is an open-hearth steel.

"It will be observed that the agreement in the results on phosphorus obtained by the different chemists is very good. The exceptions are the No. 3 steel, which contains arsenic in considerable amount, and where the discrepancy is 0.009 per cent., and in the No. 4 steel, where the discrepancy is 0.007 per cent. Considerable work was done on the No. 4 sample, in an effort to reconcile discrepancies, and it was found that the turnings from this

sample were irregular, and that two different bottles of the sample gave different results. The average of six determinations from one bottle was 0.1057, and the average of five determinations from another bottle was 0.0964 per cent. Furthermore, siftings from quite an amount of the turnings gave 0.140 per cent."

But these methods are long and laborious. It would be impossible with the most rapid of them to get a result in much less than a day, while two days would certainly be required for some of the others. Accordingly, since the demand for rapid phosphorus determinations during the last ten or fifteen years has been very great, an enormous amount of work has been done in trying to meet this demand. Modification after modification has been introduced, and paper after paper published on the subject. It is perhaps not too much to say that few chemical journals that publish any original work at all, have escaped three or four articles per year, on the determination of phosphorus in iron and steel, or on some phase of a rapid method for such determination. The result of all this work has apparently been constantly increased rapidity, with constantly greater approximations to accuracy. The present state of the matter is perhaps best shown by 'Thackray' in his paper, "A Comparison of Recent Phosphorus Determination in Steel." This writer sent to some twenty-three different chemists borings from two different samples of steel, with a request to have the phosphorus determined in each sample, and a description of the method used sent with the results. Each chemist was told that samples had been sent to others, but no attempt was made to have any special method used. The chemists embraced a professor in a technical school, the chemist of a large consumer, a number of commercial chemists, and a number of chemists employed by steel and iron works. On one sample thirty-six different results were sent in, and on the other thirty-eight. Twenty-seven different methods were employed, some of the chemists sending in results by two, and even three methods, and some sending duplicate determinations. The results obtained were obtained as follows, the figures being percentages of phosphorus in the steels :

<sup>1</sup> *Trans. Am. Inst. Min. Eng.*, 25, 370.

Sample.	1.	2.
Average of all determinations.....	0.0496	0.0835
Highest result.....	0.055	0.091
Lowest result.....	0.045	0.076
Maximum difference.....	0.010	0.015

The methods employed may be divided on the basis of time required into three classes:

1st. Those which may be called rapid, and which give a result in two hours or less.

2nd. Those which may be called slow, and which require considerably more than two hours, but still give a result the same day.

3rd. Those which may be called very slow, and which do not give a result until the second day or later.

Thirteen results on each sample were given by "rapid" methods, eleven on the No. 1 sample, and twelve on the No. 2 sample by "slow" methods, and twelve on the No. 1, and thirteen on the No. 2 by "very slow" methods. Arranging the results in accordance with this classification of the methods (and we have some very interesting data), the figures being as before, the percentages of phosphorus in the two steels are:

	Rapid methods.		Slow methods.		Very slow methods.	
	1.	2.	1.	2.	1.	2.
Average of all determinations	0.0499	0.0840	0.0490	0.0826	0.0496	0.0837
Highest result .....	0.054	0.091	0.052	0.086	0.055	0.089
Lowest result.....	0.045	0.078	0.046	0.076	0.046	0.078
Maximum difference .....	0.009	0.013	0.006	0.010	0.009	0.011

To our minds these figures are very impressive. It is worthy of note—

1st. That the average results given by the "rapid" methods only differ on either steel from the averages given by the "slow" or "very slow" methods, by a little over 0.001 of a per cent.

2d. That the maximum difference between the highest and lowest results given by the "rapid" methods on either steel is but a trifle greater than is shown by the "slow" or "very slow" methods.

In other words, if we interpret these results correctly they show that the rapid methods for determining phosphorus in steel now known and in use in many laboratories give results that are well nigh as accurate and reliable as those yielded by the longer and more laborious methods, and it must not be forgotten that

although we have placed two hours as the time characterizing a rapid method, a number of the results given above were obtained by the use of methods which give a single determination in forty-five minutes, and enable one operator to make twenty phosphorus determinations in a day. We are frank to say we do not believe such a showing would have been possible five years ago.

But these results still leave something to be desired. The discrepancy between the highest and the lowest result, is still too great. It is, perhaps, a little hazardous to place limits, but we do not think the chemists of the country should be satisfied until they are in possession of a method or methods which are so carefully worked out and so well described that in the hands of different chemists of good, fair ability and experience, results will be obtained by all, when working on the same steel, that will not differ from each other more than 0.003 per cent. The Sub-committee on Methods of the International Committee on Standards for the Analysis of Iron and Steel before referred to, have had in hand now for some two years, studies on a rapid and accurate method for the determination of phosphorus in steel. It has been the hope of the sub-committee that the ideal above given would be attainable by this method. In reality, the work of the sub-committee has embraced an examination of almost every chemical point involved, taking very little if anything for granted, and checking and proving every step. The work is not yet quite ready for publication, one or two points remaining which are not entirely settled, and it has been deemed advisable to withhold the method until these are completely cleared up.

Some years ago, with the publication<sup>1</sup> of what is commonly known as Ford's method, the determination of manganese took a decided step forward, at least in this country, so far as speed is concerned. Previous to that time the long and laborious acetate method which involved the separation of the iron from the manganese as basic acetate and subsequent precipitation of the manganese by means of bromine or as pyrophosphate, had held full sway. Ford's contribution consisted, as is well known, in separating the manganese from hot nitric acid solution of the iron or steel, by means of potassium chlorate, and Williams'

<sup>1</sup> *Trans. Am. Inst. Mining Eng.*, 9, 397.

<sup>2</sup> *Trans. Am. Inst. Mining Eng.*, 10, 100.

added the modification, now in common use, of determining the separated oxide of manganese, by its action on a standard solution of ferrous sulphate or oxalic acid. This method as now worked in many laboratories, gives a single result in forty minutes and two in an hour, and enables one operator to turn out twenty to twenty-five determinations in a day. The accuracy of this method has been questioned. We are not aware of any recent symposium on manganese, where different chemists using different methods, have worked on the same steels. In our hands this method gives results closely agreeing with check work done by the more laborious and generally accepted accurate methods, provided the sample contains not more than three-fourths of a per cent. On samples containing over one per cent. of manganese, the results are apt to be low, owing probably to the fact that the manganese does not separate from the nitric acid solution as manganese dioxide, but as some other oxide, whose composition is not positively known. In the calculation it is customary to regard the separated oxide as manganese dioxide, and this leads to perceptible error on large amounts. Producers and consumers rarely contend much over manganese in steel, and methods for its determination have perhaps not received, on that account, all the attention they deserve. There is evident need of more work on this subject.

The methods for the determination of silicon can hardly be regarded as in a perfectly satisfactory condition. If evaporation to dryness to render silica insoluble, is employed, the time required is considerable. If dehydration by means of sulphuric acid and heat, as suggested by Drown<sup>1</sup> is employed, there are difficulties which interfere somewhat with accuracy. There seems little doubt, but that in skilled hands, with sufficient care taken in the manipulation, a couple of determinations may be made on the same sample, using Drown's method, that will agree closely with each other, and with results given by the longer and more laborious methods. On the other hand, where one operator is making a number of determinations at the same time, there is much danger of error, due either to failure to dehydrate sufficiently or to overheating, resulting in the formation of insoluble iron salts. Our experience indicates that the margin between

<sup>1</sup> *Trans. Am. Inst. Min. Eng.*, 7, 346.



these two extremes is not very wide, and that it is fully as frequent to have duplicates on the same sample disagree as to agree. Our observations point to the view that the difficulty of insufficient dehydration is due to the separation of iron salts, as the sulphuric acid concentrates. These salts enclose gelatinous silica, and prevent the dehydrating acid from getting at it. Unless great pains are taken, therefore, to secure this contact by sufficient stirring, the results will be low. If by some modification the iron salts could be kept in solution until the silica is rendered quite insoluble, it would apparently be a decided step forward with this method. It may not be amiss here to call attention to the fact first noticed in the laboratory of the Pennsylvania Railroad Company,<sup>1</sup> that after the dehydration and subsequent dilution are finished, if an interval of a few hours is allowed to elapse before filtration, the silica will redissolve and the results be low. Apparently as we are able to work the method, the silica is not completely dehydrated, but only sufficiently so that if filtered at once, fairly accurate results will be obtained.

It is difficult to say anything positive about the speed and output of Drown's method. It is probably safe to say that a couple of determinations could be made in an hour and a half, but, on account of the difficulty mentioned above, the method does not lend itself well to working on a large number of samples at once, and consequently a large daily output is somewhat interfered with.

It must also be said of the methods for the determination of sulphur in iron and steel, that those most in use are hardly as satisfactory as could be desired. The studies of Phillips<sup>2</sup> conclusively show that when using the evolution method, the whole of the sulphur content is not given off in such a form as to be retained by the usual means employed to catch the gas. It seems not too much to say that it is hazardous to use the evolution method on pig or cast iron, even when fusion of the residue is employed. The formation of unoxidizable gases containing sulphur, in the application of the evolution method to steel, has

<sup>1</sup> Address to the members of the Chemical Section of the Engineers' Society, at Pittsburgh, September 27, 1892, by C. B. Dudley, on "Discrepancy in Chemical Work by Different Workers."

<sup>2</sup> This Journal, 17, 891.



not, so far as our knowledge goes, yet been demonstrated, and accordingly the evolution method is still used largely on steels. But on pig and cast irons the oxidation method seems the only one applicable and some recent studies of Blair, described in a paper at this meeting,<sup>1</sup> indicate that on certain pig irons, all the sulphur is not given, even by this method, unless the graphitic residue is fused with sodium carbonate and niter. Both methods are somewhat slow, and there is need of further study. If some means could be found by which barium sulphate could be readily and accurately converted into sulphide so that a volumetric method could be applied to this sulphide, it would be a decided step forward. The necessity in accurate work for purifying barium sulphate, as first obtained from almost any solution, by fusion and reprecipitation, adds quite considerably to the time required. With steels and two sets of evolution apparatus, using bromine for oxidation, two determinations may be made in two hours. With four sets of evolution apparatus, one operator can make twelve determinations in a day. In these cases purification by fusion is not attempted. By the oxidation method on pig or cast iron, two determinations require about five hours, while one operator with a supply of borings ahead and sufficient appliances, can get from ten to twelve results in a day. With this output, purification by fusion is not attempted. If this is done, the time for a pair of determinations must be extended an hour and a half, and the daily output would be cut down at least a third.

From what has preceded in this hasty and necessarily imperfect survey of a portion only of the analytical methods in use in the iron and steel industry, it is clearly evident that there still remains an enormous amount of work to be done in connection with methods. We have touched upon only five of the fifteen or twenty constituents occurring in and affecting the quality of iron and steel, and find the methods for determining even those more or less imperfect, and needing more work. What will be our condition as chemists if, as seems probable, nickel, chromium, aluminum, tungsten, and the gases, oxygen, hydrogen, and nitrogen, either free or combined, within the next few years, come into prominence as constituents of iron and steel, and are made elements in important commercial contracts? Still further, thus

<sup>1</sup> See page 114 of this issue.

far our methods are concerned almost entirely with the total content of the various constituents we are determining. We know very little about the compounds of the various constituents occurring in iron and steel, with the metal or with each other. Is the phosphorus present as phosphide or phosphate, or both? How besides as sulphide does the sulphur occur? Do the various carbides which are revealed by the microscope, and which are believed to be so closely dependent on the heat treatment which steel receives, and which are so intimately related to the value of the metal, differ from each other in carbon content, or only in crystalline form? Who will be the first to isolate any of these carbides? Who will first give us a practicable, accurate and sufficiently rapid method for determining oxides in steel? Who will first completely investigate the relation between the chemistry and the chilling properties of cast iron? And who will first give us a study on the form in which nitrogen occurs in this metal, and a sufficiently rapid and accurate method for its determination? Truly the harvest of chemical work before us in connection with iron and steel is bounteous. Will the laborers be forthcoming to gather the harvest?

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[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CINCINNATI.]

## **XLIX. SOME PECULIAR FORMS OF IRON.**

BY T. H. NORTON.

Received January 18, 1897.

I HAVE recently had occasion to examine two rather odd forms of iron, the peculiarities of which are sufficiently marked to warrant a brief note. The first of these is a sample from a mass of pig iron taken from a deep crevice in the hearth of a blast furnace at *Ætna*, Tenn., after the furnace was blown out. The conditions were such that the iron had been maintained in the molten condition for over a year, and had then cooled and solidified very slowly.

In appearance the sample is of a light, silvery color, and exhibits a most marked crystalline structure, with rectangular cleavage. Despite this crystalline character, it is the reverse of brittle, and shows a high degree of malleability, fragments being easily flattened out with a hammer. The drill makes but slight

impression on it. Portions were tempered and then the attempt was made to pulverize them; a slight crumbling was manifested at first, but after a few strokes of the hammer they became perfectly malleable. The piece could be split easily with a chisel, especially along the lines of cleavage. Small cubical fragments detached by this means and hammered out so as to form very thin plates, were used as material for analysis, as drillings could not be secured. Even in this form, solution was effected very slowly.

Manganese was determined by Volhard's titration method; silicon by Drown's method; sulphur by the cadmium chloride method followed by titration with iodine; phosphorus by Handy's method; and carbon by the Dudley and Pease standard method. The following results were obtained:

	Per cent.
Manganese .....	0.0362
Silicon .....	0.0262
Sulphur. ....	0.0106
Phosphorus .....	0.8285
Carbon.....	0.1035

It will be seen that the sample would be nearly pure iron, but for the phosphorus present, this being the only serious impurity. It is probable that the peculiarities above noticed are due to this unusual combination, although the very slow cooling may have influenced the crystalline condition.

The second specimen is the result of the prolonged action of the inner part of a non-luminous Bunsen flame on ordinary steel. It has served to support the mantle of an Auer von Welsbach lamp, which has been in steady use for two years, and has been exposed during this period to the combined action of a high temperature and the gases of the inner cone of the flame. As a result it has become so brittle that the upper half crumbles as easily as chalk. The lower portion, less exposed to the flame, is covered with a brittle layer, while the central core is still pure steel. Carbon determinations by the Dudley and Pease method were made of both the original steel and the brittle portion. The latter, although finely divided, required nearly a week for complete solution. The figures obtained were:

	Original steel. Per cent.	Altered portion. Per cent.
Carbon .....	0.6423	0.0978

About six-sevenths of the carbon had disappeared. Whether this loss alone can account for the peculiar structural change in the steel would seem doubtful.

I am indebted to Mr. B. R. Haile for assistance in the above analyses.

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[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CINCINNATI.]

## L. A TUNGSTEN-IRON ALLOY.

BY T. H. NORTON.

Received January 18, 1897.

THE nature and composition of tungsten-iron alloys has formed the subject of several papers published during the past few years. As an additional contribution to the literature of the subject, the following brief note of the examination of a commercial alloy may be of interest.

The alloy in question was introduced commercially on account of its extreme hardness. The specimen examined was of a lustrous appearance, except in places where it was coated with a yellowish-green incrustation. A large number of blow-holes were observed. The hardness was about 7, quartz being scratched with some difficulty. The material was quite brittle, being easily shattered with the hammer. The small pieces were powdered with some difficulty in an agate mortar. The specific gravity of the powder was 14.55.

The method of analysis employed was that recommended by Ziegler,<sup>1</sup> which consists essentially in fusion with sodium nitrate in a silver crucible, and subsequent precipitation of the tungsten as mercurous tungstate.

The results obtained were as follows :

	I.	II.
Tungsten.....	93.22	93.43
Iron.....	6.08	6.18
	<hr/> 99.30	<hr/> 99.61

Mr. D. M. Roth assisted in the analysis of this alloy.

<sup>1</sup> *Ding. poly. J.*, 274, 513.

## NOTE ON AN IMPROVED SPECIFIC GRAVITY BOTTLE OR PYKNOMETER.<sup>1</sup>

BY EDWARD R. SQUIBB.

Received January 11, 1897.

THE first attempt of the writer to improve the ordinary specific gravity bottle was described and illustrated in a paper published in the *Ephemeris*, 1, 11, for September, 1883, p. 349. The next improvement, wherein the principle of the present bottle was first applied, was described and illustrated in the *Ephemeris* for May, 1884, 2, No. 3, p. 528. The next improvement was described and illustrated in the *Ephemeris* for July, 1889, 3, No. 4, p. 1162.

The present form, now to be described and illustrated, has been in use during the past five years with very satisfactory results.

The increasing importance of specific gravity of liquids, and the increasing frequency with which close determinations are required, make any improvement that can be suggested in the apparatus worth describing.

Different authorities give different temperatures, not only for the standard unit water volume, but also a different temperature of the compared volume from the standard volume. The standard volumes most commonly used are 0° C., 4° C., 10° C., 15° C., 15.6° C. = 60° F., 20° C., and 25° C. = 77° F., and it is very convenient to have a single bottle in which the standard water volume can be accurately measured at all these temperatures, and in which liquids can without loss be brought to room temperature for weighing. As the bottles illustrated on p. 113 accomplish these objects easily and accurately they are supposed to be improvements on the older form of bottles.

The control of error by expansion of liquid before weighing has recently been effected by Mr. J. C. Boot in his "New Form of Pyknometer," presented at a meeting of the New York Section of the American Chemical Society, held November 6, 1896.<sup>2</sup> In this bottle change of temperature is controlled by having the bottle made double with a vacuum interspace. But this bottle can be used only at a single standard unit water volume, and the provision by which change of temperature is prevented, also

<sup>1</sup> Read before the New York Section of the American Chemical Society, at the meeting of January 8, 1897.

<sup>2</sup> See this Journal, January, 1897, p. 61.

prevents change in adjusting to standard temperature so that this adjustment has to be made before the liquid is put into the bottle, whereas in the improved bottle shown here any temperature of unit volume below  $25^{\circ}$  C. may be used, temperatures being always adjusted in a bath.

By the adjoining cut it will be seen that the mechanical construction is that of an ordinary thermometer, and as far as temperature is concerned, the principle of action is the same. It therefore has a thin light bulb (the bottle), a graduated stem, and a safety reservoir, the graduated stem being ground into the bottle for facility of filling and emptying. The graduation of the stem is arbitrary, and may be 0 to 50 or 0 to 100.

The use of the bottle and its parts will be easily understood from a description of its adjustment. As received from the glass blower the chemically cleaned and tared bottle should hold say 100 grams of recently boiled distilled water at  $20^{\circ}$  C. at about fifty-eight divisions of a scale of 0 to 100. In weighing 100 grams of water into the bottle the fine adjustment to 0.001 gram is made by very narrow strips of blotting board that will pass easily down the bore of the graduated stem and absorb minute quantities of liquid. When the 100 grams are in the bottle and the column stands at say 50 to 65 divisions of the scale, the little stopper is put in at the top and the leaden weight is put on the neck, and the whole is immersed in a bath at  $0^{\circ}$  C. until the column of water in the stem ceases to fall. It should then read at 0 or not much above it and the reading be noted. If it reads below 0 the bottle is too large and the stopper part of the stem must be ground farther into the bottle neck, until the reading on new trials brings the column above 0 at  $0^{\circ}$  C. Then the bottle is put into a bath at  $25^{\circ}$  C. and kept there with stirring of the bath until the column ceases to rise, when it should read somewhere from 90 to 100 of the scale. Should it read above 100 of scale, while the lower limit is far above the 0 of scale, then the bottle is too small and the end of the stopper must be ground off until the reading of the column is within the scale at both ends of the scale.

The 100 gram bottle figured in the illustration is one that has been many years in use, and during the first two years the column moved up as it will do in thermometers, but of late



The small stoppers have a minute air passage through the center that could not be shown in the cut.

IMPROVED SPECIFIC GRAVITY BOTTLE, OR PYCNOMETER.

years it has been constant. This bottle has the following scale readings when it contains 100 grams of recently boiled distilled water :

When the column has ceased to move at	4° C.	the reading is	6.0
" " " " " " " "	10° C.	" "	10.5
" " " " " " " "	15° C.	" "	28.0
" " " " " " " "	15.6° C.	" "	31.0
" " " " " " " "	20° C.	" "	57.5
" " " " " " " "	25° C.	" "	97.5

With such a bottle, specific gravity of liquids can be taken at any of the temperatures of the standard unit volume, to the sixth decimal place. But such accuracy is almost valueless if both

temperatures be not expressed. Fortunately this good practice of always giving both temperatures, as  $\frac{1}{4}^{\circ}\text{C.}$ ,  $\frac{1}{2}^{\circ}\text{C.}$ ,  $\frac{1}{8}^{\circ}\text{C.}$ , is now becoming common.

## THE DETERMINATION OF SULPHUR IN PIG IRON.

BY ANDREW A. BLAIR.

Received January 8, 1897.

**T**HERE are two general methods in use for the determination of sulphur in pig iron; the evolution method and the oxidation method. Attention has been repeatedly called to the fact that the residue from many pig irons after treatment with dilute hydrochloric acid contained sulphur, while in some the aggregate evolved as hydrogen sulphide and remaining unacted on in the residue was decidedly less than the amount obtained by the oxidation method. The cause of this discrepancy has been clearly pointed out by Prof. Phillips<sup>1</sup> in his admirable paper on the "Evolution Method for the Determination of Sulphur in White Cast Iron."

Following the line of Prof. Phillips' work I found that it was possible to convert all the volatile sulphur compounds into hydrogen sulphide by passing the evolved gases mixed with hydrogen through a tube filled with pumice and heated to redness. The long boiling that proved necessary and the passage of so much distilled hydrochloric acid and water through the red hot tube made the method too troublesome for ordinary use.

During this investigation I received a sample of pig iron for the determination of its sulphur contents, and used for this purpose not only the oxidation method but the new method as well. The results were as follows:

	Per cent.
1. Sulphur by oxidation.....	0.032
2. Sulphur evolved as hydrogen sulphide.....	0.000
3. { Sulphur obtained as hydrogen sulphide after passing	
{ through red hot pumice .....	0.005
{ Sulphur obtained by fusion of residue.....	0.057
Total sulphur .....	0.062

This seemed to point to the fact that the ferric chloride in the oxidation method held barium sulphate in solution. Mr. P. W.

<sup>1</sup> This Journal, 17, 891.



Shimer made a careful determination of sulphur in this sample by the oxidation method and obtained 0.042 per cent. I repeated all my determinations but the results remained the same. I then made a determination by Bamber's method<sup>1</sup> and found 0.064 per cent. Finally, I fused the residue of carbon, silica, etc., filtered off before precipitating the sulphuric acid in the oxidation method, and obtained 0.030 per cent. sulphur unacted on by hydrochloric and nitric acids. Mr Shimer corroborated these results. In other words, we now have in pig irons :

1. Sulphur evolved, by solution of the iron in hydrochloric acid as hydrogen sulphide.

2. Sulphur evolved as other compounds not absorbed by alkaline lead salts or oxidized by bromine or potassium permanganate.

3. Sulphur in some form, unacted on by boiling hydrochloric acid, but oxidized by nitric acid or aqua regia.

4. Sulphur in some form, unacted on by nitric acid, hydrochloric acid, or aqua regia.

The simplest and most satisfactory method for the treatment of pig irons containing sulphur in the latter form is that of Bamber. It is essentially as follows: Dissolve five grams or a five factor weight (6.878 grams) in strong nitric acid, add two to five grams of potassium nitrate, evaporate to dryness in a platinum capsule and ignite. Treat with water with the addition of a little sodium carbonate, filter, and wash with water containing sodium carbonate. Acidulate with hydrochloric acid, evaporate to dryness, redissolve in water with a few drops of hydrochloric acid, and precipitate boiling with barium chloride.

The pig iron referred to above contains appreciable amounts of titanium and vanadium and Mr. Shimer and I are now engaged in studying the residue insoluble in hydrochloric acid. The results of our investigation we hope will be of sufficient interest to warrant their presentation to the Society.

<sup>1</sup> *J. Iron and Steel Inst.*, 1894, 1, 319.

[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF PURDUE UNIVERSITY.]

## THE OCCURRENCE OF RAFFINOSE IN AMERICAN SUGAR BEETS.

BY W. E. STONE AND W. H. BAIRD.

Received January 12, 1897.

THE sugars first noticed in the Australian Eucalyptus manna by Mudie<sup>1</sup> and by Johnston<sup>2</sup> and called melitose<sup>3</sup> by Berthelot ; later identified in the cottonseed as gossypose by Boehm<sup>4</sup>, and finally in molasses and refinery products of the sugar beet and called raffinose by Loiseau<sup>5</sup>, have been shown to be identical with each other. Raffinose has also been found in barley,<sup>6</sup> and in wheat,<sup>7</sup> and is thought to be present in many other plants.<sup>8</sup>

Raffinose, as a distinct kind of sugar, belongs to the not numerous class of tri-saccharides with the formula  $C_{18}H_{32}O_{16}$ . By hydrolysis, its molecule becomes decomposed, forming one molecule each of dextrose, levulose, and galactose.

Its properties have been thoroughly studied and are probably as well understood as those of most of the more common sugars.

Of particular interest is its occurrence in the residual and secondary products resulting in the manufacture of beet sugar. Here it crystallizes with cane sugar, modifying the crystalline form of the latter and increasing the specific rotation markedly. These two properties actually led to the discovery of raffinose in beet sugar products, where its presence for a long time introduced serious and unexplainable errors into the analytical operations of the sugar factory and refinery.

The frequent occurrence of raffinose in the refinery products from beet sugar, and especially those which have been subjected to any of the methods involving the use of strontia, baryta, or lime for the separation of the sucrose from the uncrystallizable molasses, led to the belief that raffinose was a secondary product derived from sucrose or some other sugar in the course of these

<sup>1</sup> *J. de Pharm.*, II, 12, 705.

<sup>2</sup> *J. prakt. Chem.*, I, 29, 485.

<sup>3</sup> *Ann. chim. phys.*, III, 46, 66.

<sup>4</sup> *J. prakt. Chem.*, II, 30, 37.

<sup>5</sup> *Journal des Fabricants de Sucre*, 24, 52; 26, 22, etc.

<sup>6</sup> O'Sullivan : *Chem. News*, 52, 393.

<sup>7</sup> Richardson and Crampton : *Ber. d. chem. Ges.*, 19, 1180.

<sup>8</sup> Scheibler : *Neue Ztschr. für Rübenzuckerindustrie*, 23, 237.

operations and that it was not originally present in the beet juices.

It has, however, been conclusively shown that raffinose is a natural constituent of the sugar beet, from which it has been separated directly by Von Lippmann,<sup>1</sup> and the impossibility of any transformation of sucrose into raffinose by heating with alkalies, has been shown by the investigations of Tollens<sup>2</sup> and others.

The quantity of raffinose in beet juice is, however, very small, amounting to from 0.01 to 0.02 per cent. In beet molasses two to three per cent. of raffinose has been observed, and in various concentrated products of molasses refineries, as high as sixteen per cent. has been noted.

Attention has been called to the fact that the amount of raffinose found in sugar beets, is dependent on climate, soil, seed, conditions of growth, etc., and varies between wide extremes. It might, therefore, reasonably be expected that under some conditions this minor constituent of the sugar beet would be lacking entirely.

The conditions under which sugar beets are grown in America must differ in many respects from those of Northern Europe and many of the observations recorded in the latter country may well be subjected to verification here.

On this account it seemed desirable to ascertain definitely whether raffinose occurs in the products of the American beet.

The attention of one of us was called to certain phenomena observed in the works of the Norfolk Beet Sugar Co., at Norfolk, Neb., and an investigation of the same has furnished the data for this paper.

The process of making sugar from beet juices, as carried on at the Norfolk works, involves the following special operations :

After the clarification, concentration, and crystallization of the beet juices, the uncrystallizable residue is returned to the beginning stages of the process and boiled again with fresh beet juice constituting what is known as a "mixed pan."

This is boiled "to grain," *i. e.*, to such concentration that crystals begin to form, and is sent to the "crystallizer," where,

<sup>1</sup> *Ztschr. des Vereins f. Rübenzuckerindustrie*, 39, 880.

<sup>2</sup> *Ztschr. des Vereins f. Rübenzuckerindustrie*, 39, 921.

being slowly agitated under carefully controlled temperature for about twenty-four hours, an increased crop of crystals is obtained. The molasses remaining at this state is treated by the Steffen's process,<sup>1</sup> which consists essentially in precipitating the sugar from a diluted solution of the molasses, by adding finely powdered quicklime at a temperature of 8° to 12° C.

This product consists in the main of mono- and dicalcium saccharates,  $C_{12}H_{22}O_{11}CaO$  and  $C_{12}H_{22}O_{11}2CaO$ .

These saccharates are mixed with fresh beet juices, and boiled in the "clarifiers" and by subsequent carbonation are decomposed. The sugars thus liberated become mingled with a new portion, fresh from the beets. It will be observed that the same particles of sugar, if they fail to crystallize, may repeatedly pass through this cycle of operations, being recovered finally in the form of saccharates and returned to the beginning of the process.

If now we bear in mind that raffinose behaves like sucrose in many respects, especially toward the alkaline earths, with which it forms insoluble compounds, both in hot and cold solutions, we shall readily see how the small amount originally present in the beet juice may accumulate in the molasses and secondary products of the factory. This tendency is increased by the fact that this sugar would, to a large extent, remain uncrystallized in the presence of a much larger proportion of sucrose, and so at the close of the campaign, practically all of the raffinose present in the entire amount of beets which have been handled during the season may be found in the molasses and second grade sugars which are being repeatedly passed through the cycle of operations described.

If, as has been noted, the amount of accumulated raffinose reaches eight to twelve per cent., or even less, it not only destroys the accuracy of all polarimetric determinations of the purity and concentration of the various secondary products of the factory, but also seriously retards the crystallization of the sucrose itself.

For instance, the presence of even two per cent. of raffinose causes an apparent difference in the purity of the molasses sufficient to determine whether it is to be returned to the pan or be

<sup>1</sup>Stammer: Zucker Fabrikation 1887, 1,047.

sent to the Steffen's process. It is evident, therefore, that successful factory practice may be seriously interfered with if this source of error is ignored.

During the campaign of 1894 and 1895 at the Norfolk factory, it was noticed that the purity coefficient of syrups from the crystallizers, as determined by polarimetric operations, gradually increased, while crystallization seemed to be more and more retarded.

These phenomena could be reconciled with each other only on the assumption of the presence and constant increase of raffinose. Similar observations followed in 1895 and 1896 and it was also observed that the sugar from the crystallizer frequently contained ragged and elongated crystals of abnormal appearance. Frequent inversion tests, according to Creydt's<sup>1</sup> method, indicated the presence of about three per cent. of raffinose, which gradually increased toward the end of the season. On the other hand, attempts to produce mucic acid from the syrups by oxidation with nitric acid, according to Tollen's method, repeatedly failed.

These results, indicating in part the presence of raffinose, seem to render it desirable to undertake the systematic examination of molasses from the "crystallizer," with the object of separating, purifying, and identifying the raffinose, if it should prove to be present. At this time the investigation was transferred to the chemical laboratory of Purdue University.

Renewed attempts to detect raffinose by means of the mucic acid tests were made as follows :

Several ten-gram portions of syrups were oxidized with nitric acid of specific gravity 1.15, according to prescribed methods. Oxalic acid crystallized abundantly from these solutions but no mucic acid could be obtained under these conditions.

Again, to a similar portion of syrup was added so much milk sugar as would yield an amount of galactose equivalent to three per cent. raffinose and this mixture was oxidized in the usual way. This also yielded no mucic acid. The same amount of milk sugar, oxidized in aqueous solution under the same conditions, gave an abundance of mucic acid.

These results illustrate well the unreliability of the mucic acid

<sup>1</sup> *Deutsche Zuckerindustrie*, 11, 757, and 13, 582, etc.

test for raffinose when applied to complex mixtures of salts and organic matters, of which the beet molasses furnishes a good example. Mucic acid was undoubtedly present, as subsequently shown, but was probably held in solution in the form of soluble salts.

Accordingly, steps were taken to separate the sugars in the molasses from other materials with a view of applying the mucic acid test to them directly. This was accomplished by treating about 200 grams of the syrup with an excess of basic lead acetate by which a dense precipitate was thrown down. The liquid was filtered and treated with ammonia until it was strongly alkaline. This produced a second precipitate consisting of lead compounds of sugars. This was filtered, suspended in water, the lead removed with hydrogen sulphide, and the filtrate evaporated to a syrup. To this syrup was added nitric acid of specific gravity 1.15 and the mixture heated in the usual way prescribed in making mucic acid tests.

After three days an abundance of a white crystalline powder separated from the solution, which, after washing and drying, was found to have a melting-point of  $213^{\circ}$  C., showing it to be mucic acid. This may be regarded as a fairly conclusive qualitative proof of the presence of raffinose in the material studied. Nothing short of the actual separation of sugar in pure form and the determination of its constants, can be accepted, however, as conclusive proof of its presence. Numerous methods have been proposed for the isolation of raffinose from mixtures with other sugars and substances.

Most of these methods are based on the insolubility of raffinose in combination with certain metallic oxides as well as its unusual solubility in absolute methyl alcohol. Following any of these methods, however, its separation is acknowledged to be a tedious operation. Our experience in this attempt included many separate methods and operations, from which it will suffice to mention the following:

We first followed the directions of Kodyl,<sup>1</sup> by which the impurities of the syrup are precipitated with basic lead acetate and from the resulting filtrate, the sugars are thrown down by the addition of ammonia.

<sup>1</sup> Oesterreichisch-Ungarische Zeitschrift f. Zuckerindustrie u. Landwirtschaft, 20, 700, and 21, 92.

From this compound of lead and sugars, the latter are liberated by treatment with carbon dioxide or with hydrogen sulphide, and the solution thus obtained may be concentrated to a point of crystallization. Pursuing this method, we were able to obtain a small amount of sugar crystals which had the appearance of raffinose but which were accompanied by other materials of a gum-like nature which prevented their separation in the pure form.

We next employed the method proposed by Scheibler<sup>1</sup> which is based on the principle that strontium oxide throws down sucrose from a cold solution, but in a hot solution will precipitate both sucrose and raffinose. A twelve per cent. solution of about 300 grams of syrup received as much finely powdered strontium oxide as would be dissolved. After standing forty-eight hours, the filtrate received an additional amount of strontium oxide and was boiled for thirty minutes. An abundant precipitate resulted, which was suspended in water and decomposed by means of carbon dioxide. The filtrate from this which was supposed to contain raffinose and sucrose, was evaporated to a syrup, absorbed in dry sand, thoroughly dried and extracted with absolute methyl alcohol, but we were unable to obtain raffinose crystals from the product.

We finally made use of the following method which is a combination of the preceding ones and which proved successful.

2000 grams of syrup were freely diluted with water and treated with basic lead acetate in large excess. Neither sucrose nor raffinose form insoluble compounds under these conditions but a large amount of other material was precipitated from which the solutions were decanted, and after still farther dilution, were treated with ammonia until strongly alkaline. After standing in a warm place some forty-eight hours, a heavy precipitate had settled to the bottom of the vessels. This precipitate is supposed to consist of compounds of one molecule of raffinose or sucrose respectively, with three molecules of lead oxide. This was washed by decantation, suspended in water and treated with sodium carbonate and carbon dioxide until all of the lead had been removed. The filtrate therefrom was concentrated to a thin syrup. It was examined with the polarimeter and estimate made

<sup>1</sup> *Ber. d. chem. Ges.*, 18, 1409.



of the amount of sugar it contained, calculated as sucrose. Strontium oxide was added in the proportion of three molecules to one of sugar and the mixture maintained at a temperature of boiling water for three hours, during which a fine, yellowish white, granular precipitate was thrown down. This presumably consisted of strontium saccharate and raffinosate. It was noted in this and subsequent operations that it was not possible to remove all of the sugar from the solution by this process since the filtrate from these combined strontium compounds, invariably possessed a rotatory power equal to about two to four per cent. of sugar. The strontium compounds thus obtained were decomposed by treatment with carbon dioxide; the solution filtered off and concentrated to a thick syrup. After forty-eight hours, fine crystals could be seen under the microscope, and after a week, the mass had become solid. These crystals were long and needle-like when seen under the microscope. To the naked eye they presented a silky, shimmering appearance, often gathered in bunches radiating from a common center. No crystals resembling sucrose crystals could be observed. After being thoroughly dried, these crystals showed a specific rotation of  $74^{\circ}$ . That of pure raffinose is  $104^{\circ}$  to  $105^{\circ}$ . Of pure sucrose  $66.5^{\circ}$ . These results indicated a mixture of which the greater portion was probably sucrose, although the increased specific rotation pointed to the presence of a small amount of raffinose. Attempts were made to purify this product by extracting with absolute methyl alcohol by which about half the entire mass was dissolved. This solution, on being brought to crystallization, had every appearance of pure raffinose while the insoluble residue gave a specific rotation of pure sucrose.

This process as described was repeated several times until we had obtained what appeared to be several grams of fairly pure raffinose. But while these crystals were invariably of the general superficial character peculiar to raffinose, it was found that the specific rotation of all the different preparations was very far from being that of the sugar sought, varying from  $72^{\circ}$  to  $85^{\circ}$ . The different portions were therefore combined and subjected to repeated extraction with boiling methyl alcohol. These extracts, on being brought to crystallization showed, however, that the separation of raffinose and sucrose could not be accomplished in



this way, since none of the products show a specific rotation greater than  $80^{\circ}$ .

The next step was to employ cold methyl alcohol for such fractional solutions. According to Scheibler,<sup>1</sup> raffinose is readily dissolved in cold methyl alcohol, while sucrose is scarcely affected. Nevertheless, upon treating our products with cold methyl alcohol, we obtained therefrom portions which, after being crystallized, possessed respectively the specific rotation of  $78^{\circ}$ ,  $75^{\circ}$ , and  $71.5^{\circ}$ , showing that no progress had been made in the separation of the two sugars. Finally, all these products were once more combined, dissolved in water, and left to crystallize slowly. As soon as an appreciable amount of crystals had formed in this watery solution, they were removed, dried, and polarized. Five successive fractions thus obtained showed the following specific rotations :

- I.  $(\alpha)_D = 86.7^{\circ}$ .
- II.  $(\alpha)_D = 103.7^{\circ}$ .
- III.  $(\alpha)_D = 99.2^{\circ}$ .
- IV.  $(\alpha)_D = 92.0^{\circ}$ .
- V.  $(\alpha)_D = 75.0^{\circ}$ .

Of these portions, evidently Nos. II and III were practically pure raffinose. Nos. I and IV were united and subjected to a second fractional crystallization, from which was obtained one small portion which showed a specific rotation of over  $100^{\circ}$ .

From these results we feel justified in concluding that raffinose occurs in the juices of the American sugar beet in appreciable quantities.

Certain peculiarities observed in connection with the crystallization of these mixtures of sucrose and raffinose, seem to be worthy of special mention.

The influence of small amounts of raffinose upon the form of sucrose crystals has been much commented on and investigated. In general, it is well understood that the presence of raffinose in cane sugar tends to produce elongated, sharp-pointed abnormal crystals. But the microscopic aspect of the crystals of such mixtures has been only rarely referred to and, so far as we know, not figured.

In the course of our investigation we had frequent occasion

<sup>1</sup> *Ber. d. chem. Ges.*, 19, 2868.

to examine preparations of our products under the microscope, and were repeatedly surprised to observe that solutions containing apparently but a very small amount of raffinose, would completely crystallize under the microscope into forms which could scarcely be distinguished from pure raffinose.

The accompanying illustrations demonstrate this tendency far better than any mere description.

No. 1 shows the normal form of the crystals of pure sucrose seen under the microscope.

No. 2. The crystals of pure raffinose.

No. 3. The crystal form of a mixture of the two with a specific rotation of  $76^{\circ}$ .

It is to be noted that the influence of the raffinose is manifested not in the appearance of isolated raffinose crystals but in a modified and abnormal appearance of all of the crystals, which are all similar to each other but entirely distinct from those of sucrose.

This tendency on the part of raffinose to so distinctly modify the crystals of sucrose, would seem to afford a means of readily identifying the presence of small amounts of the former in mixture with sucrose.

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## OUR PRESENT KNOWLEDGE OF ARGON, WITH A PARTIAL BIBLIOGRAPHY.

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SINCE the appearance of the account by Lord Rayleigh and Prof. Ramsay, of their joint discovery, there has been evident, in this country and abroad, a general air of expectation, which even the remarkable results that have been obtained have not been sufficient to remove. In fact, instead of allaying this expectancy it has rather been increased, by the accounts of researches thus far made, so that now, even more than at first, the scientific world is looking forward to the solution of the remaining problems concerning argon, with an interest, rendered particularly intense by the commonly accepted conviction that, upon the nature of the solution will depend, in a great measure, our views of certain chemical theories which we have heretofore regarded as firmly established. While the results of the inves-

No. 1. Pure Sucrose.  
Specific Rotation  $66.5^{\circ}$ .

No. 2. Pure Raffinose.  
Specific Rotation  $103.5^{\circ}$ .

No. 3. A Mixture of Sucrose and Raffinose.  
Specific Rotation  $76^{\circ}$ .



tigations of the properties of argon fall far short of clearing up many uncertain points concerning the character of the gas, they are not without direct and important bearings on them and it is with a view of presenting and discussing the essential features of these results that this paper has been prepared.

The account of the discovery and early researches on argon, by Lord Rayleigh and Professor Ramsay, has been given such wide circulation and these have now become matters of such familiar knowledge to chemists that I will take up the time of the Society, in connection with them, only so far as is necessary to sum up their results and consider them briefly in connection with those subsequently obtained.

In order to successfully study the character of argon it was necessary, first of all, to obtain it in considerable quantities in a pure state. The first method, sometimes and very appropriately called the Cavendish method, since it is the one by means of which Cavendish isolated and measured an impurity in atmospheric nitrogen, consisted in passing electric sparks through a mixture of air and oxygen—mixed in about equal quantities—confined in a eudiometer over dilute alkali. When all of the nitrogen had combined with the oxygen and been absorbed by the alkali, the excess of oxygen was absorbed by alkaline pyrogallate, leaving the required gas free. A second method, by means of which argon could be obtained more satisfactorily and in larger quantities, consisted in passing pure dry air over red hot copper, which removed the oxygen, and then over heated magnesium, which removed the nitrogen, the inert gas being left. This process, which is here merely outlined, required a circulation of not far from two days through the system of tubes containing the absorbents before the argon could be obtained pure. The argon used in many of the most recent investigations was obtained by keeping up an electric arc in a mixture of air and oxygen for about two days, removing the nitrogen and oxygen as already described. Other methods for obtaining argon have been suggested, but their utility has yet to be demonstrated.

The proportions in which argon exists in the atmosphere was ascertained by the experiments which led to the discovery of the gas, to be about  $\frac{1}{100}$  by volume and  $\frac{1}{16}$  by weight. The most

recent investigations on this point are those of Th. Schloesing,<sup>65</sup> who has found that the proportion of argon in atmospheric nitrogen is 0.0119, a result which agrees to a remarkable degree with those obtained by Rayleigh and Leduc. Schloesing has further shown<sup>66</sup> that in the case of argon, as with oxygen and nitrogen, its proportion in the atmosphere varies to a degree scarcely perceptible on analysis. Kellas, who has made researches along somewhat the same line as those of Schloesing, has found<sup>67</sup> that argon exists in a greater proportion in respired air than in normal air. In the researches on the occurrence of argon other sources than the atmosphere have been discovered. It has been found to be given off in small quantities, in connection with other gases, when cleveite, samarskite, euxenite, and a few other minerals are treated with acids or heated *in vacuo*,<sup>68</sup> but as yet the condition in which argon exists in these minerals has not been determined.<sup>69</sup> A still more interesting source of argon is that of meteoric iron, which was found in Augusta County, Virginia. The specimen was analyzed by Prof. Ramsay and found to contain the inert gas.<sup>70</sup> Argon has been discovered in the waters of a number of mineral springs. Bouchard has found it in certain springs in the Pyrenees,<sup>71</sup> Kayser in the springs of Wildbad, in the Black Forest,<sup>72</sup> Rayleigh in the Bath Springs,<sup>73</sup> and Ch. Mouren has found that it constitutes a part of the gases which escape abundantly in bubbles from the spring of Maizières<sup>74</sup> (Côte d'Or). Bedson and Shaw have found argon in the gases enclosed in rock salt,<sup>75</sup> and Th. Schloesing has discovered it to be a constituent of fire damp and of the gas of Rochbelle.<sup>76</sup> Argon has been sought for without success in animal and vegetable substances<sup>77</sup> by Geo. MacDonald and A. M. Kellas, but Schloesing and Richard, as a result of an investigation, which shows something of the extent to which researches on the occurrence of argon have been carried, have found that it forms a part of the gases of the natatory bladder of fishes and physaliæ.<sup>78</sup>

Concerning the true character of argon there have been many and varied opinions advanced, but none so widely accepted as the one originally advanced by the discoverers of the gas, which is that it is an element and monatomic.<sup>79</sup> It has been suggested that argon might be an oxide of nitrogen, a view speedily dis-

carded when the methods of isolating argon became better understood. Another view advanced by Dewar<sup>3</sup> and others is that argon might be an allotropic form of nitrogen bearing the same relation to that element that ozone does to oxygen. This would explain the concurrent existence of argon and nitrogen, and the fact that many of the lines of their spectra are near to each other. It would also explain the inactivity of argon and would allow it a proper place in the periodic system. Against this view are the facts that in decomposing compounds of argon no nitrogen is detected and that in no way has any one succeeded in obtaining nitrogen from argon or argon from pure nitrogen, and that, if we adopt  $N_2$  as the formula of argon its density would not at all conform to the density found for argon. Further evidence against this theory is found in the results of researches by Peratoner and Oddo,<sup>55</sup> who, observing that the molecular weight of argon approximates that of a triatomic polymeride of nitrogen, made a number of experiments on a gas obtained by the decomposition of aziomide, but could find no trace of argon.

The view suggested by Crookes in his paper on the spectra of argon,<sup>6</sup> that the discoverers of argon may have added "two members to the family of elements" has been somewhat extensively adopted. This view exhibits the least incompatibility with our present theories of chemistry and, if shown to be the true one, will remove the grave suspicions which since the discovery of argon have rested on the periodic classification of the elements. The fact of the duality and simultaneous appearance of the spectra of argon, which, as Friedländer has pointed out,<sup>56</sup> has been regarded as evidence of the compound nature of the gas, cannot rightfully be so regarded since the same phenomena have been observed by W. N. Hartley in connection with nitrogen, which is of undoubted elementary character.<sup>56</sup> The observation of three different spectra of argon, by Eder and Valentia,<sup>71</sup> appears to have a very important bearing on the theory suggested by Crookes and to deserve careful consideration in forming our opinions concerning the elementary or compound character of argon.

Whatever other light spectroscopic investigations may throw upon this question, this much is certain, as Hartley has pointed

out," that since no compound gaseous substance known can withstand the temperature of the electric spark, without exhibiting the spectra of its elements, and since the spectra of argon are not those of any other known substance it follows that, if the gas is a compound; all of its constituent elements have been hitherto unknown.

The most commonly accepted view concerning argon, *vis.*, that it is an element, is based chiefly upon the evidence of its being monatomic. As pointed out in their original paper,<sup>8</sup> Lord Rayleigh and Prof. Ramsay found the ratio of the specific heats of argon to approximate 1.67, which is the theoretical ratio of the two specific heats of a monatomic gas.

In the absence of contradictory evidence, this fact would have been considered satisfactory proof of the monatomicity of the argon molecule and the consequent elementary character of the gas, but the density of argon, having been found to be approximately twenty, the atomic weight would, if the molecule contains but one atom, be forty, in which case there would be no proper place for it in the periodic system. To accept one as the atomicity of argon means the overthrow of the present classification of the elements. On the other hand, to assume that argon has an atomicity other than one, in which case it finds a proper place in Mendeléeff's system, is in direct opposition to the kinetic theory, which has not hitherto been called into question.

Still other theories have been advanced to explain the nature of argon. Nasini has suggested that it might be a diatomic gas. but with its atoms so nearly spherical as to make it resemble a monatomic gas in certain respects.<sup>40</sup> This view is thought to afford the best explanation of the peculiar character of argon by a great number of the chemists who doubt its monatomicity. Another view is that argon contains both monatomic and diatomic molecules. This view, which was referred to by Prof. Ramsay in his lecture given before the Oxford Junior Scientific Club on a recent date,<sup>78</sup> is regarded by him, as it is by chemists generally, as being improbable in the extreme.

In the investigation of the physical properties of the new gas the ground has been so thoroughly covered that we can hope for no extensive advance in this direction.

The density of argon, which it has thus far been found im-



possible to completely reconcile with its other properties, was found by Lord Rayleigh to be 19.94.<sup>67</sup> The refractivity and viscosity were found by the same physicist to be respectively 0.961 and 120, air being the standard.<sup>68</sup>

As regards the spectra of argon, the early and accurate knowledge of which has been of incalculable value to the investigators of the gas, Mr. Crookes<sup>6</sup> noticed that at the end of the capillary tube containing the argon, near the positive pole, there appeared a reddish, and at the end near the negative pole, a bluish glow, two spectra being produced, twenty-six lines of which appeared to be common.

In comparing the spectra of argon with the sharp line spectrum of nitrogen Mr. Crookes says: "The sharp line spectrum of nitrogen is not nearly so striking in brilliancy, number or sharpness of lines as those of argon, and the most careful scrutiny fails to show any connection between the spectra. I can detect no lines in common." Between the band spectrum of nitrogen and the spectra of argon Mr. Crookes observed two or three close approximations of lines, but no positive coincidences.

Eder and Valenta have observed that in addition to the red and blue spectra there is a third spectrum produced when very large condensers are used with a Ruhmkorff's coil and powerful currents employed in the primary circuit.<sup>71</sup> This third spectrum is distinguished from the other spectra in that many of the lines appear more distinct while others are less so, and by the appearance of entirely different lines as well.

In connection with the red and blue color, which Crookes has observed, it is interesting to note that, during the action of the silent electric discharge in a mixture of benzene vapor and argon, Berthelot observed an intense greenish fluorescence, and that this gave a spectrum showing lines and bands in the yellow, green, and violet, similar to those observed in the spectrum of the aurora borealis.<sup>72</sup> While none of the lines coincided exactly with the principal line of the aurora borealis, 557, the argon line 555.7, is very near the latter and Berthelot is convinced by his comparative study of the two spectra, that there is some relation between the presence of argon in the atmosphere and the production of the aurora borealis.

At the time of the discovery of argon no chemical properties

of the gas, other than its extreme inertness, had been discovered, hence the name argon, from the Greek prefix  $\alpha$ -privative meaning without and  $\epsilon\rho\gamma\omicron\nu$ , work. Although subsequent researches have shown the term to be, in a strictly literal sense, a misnomer, it is not to be overlooked that the name argon was only given after repeated attempts to induce chemical combination of the gas with other elements had been made.

The following is a list of the more important experiments made at that time and subsequently, with a view of studying the chemical properties of argon. It was mixed successively with oxygen, hydrogen, and with moist and dry chlorine and subjected to the action of the silent electric discharge without undergoing change. It was brought in contact with sulphur and phosphorus at a red heat and no change took place. Tellurium was distilled in the gas, as were sodium and potassium, without losing their luster. It was not absorbed by red hot caustic soda nor soda lime. It passed unaffected over red hot potassium nitrate and sodium peroxide. Persulphide of sodium and calcium were without action on it at a red heat. Platinum black did not absorb it nor did platinum sponge. Wet oxidizing and chlorinating agents, as potassium permanganate, aqua regia, bromine water, bromine and alkali, and hydrochloric acid were entirely without action upon the gas. It resisted the action of nascent silicon and boron, as proven by contact with a mixture of sodium and silica, and one of sodium and boric anhydride. It was subjected to the influence of the electric spark in contact with fluorine, boron, titanium, lithium, and uranium without inducing chemical action.

An apparent combination of argon and carbon was observed by Prof. Ramsay by making an arc between two rods of purified carbon in an atmosphere of argon.<sup>43</sup> Further investigation along the same line,<sup>76</sup> however, here led to the conclusion that argon does not combine with carbon even at the temperature of the electric arc and that the expansion which led to the inference that a chemical union had taken place was due to the carbon dioxide gas occluded on the surface of the carbon not being entirely removed, before the rods were introduced into the argon receiver. As further evidence bearing upon the possible union of argon and carbon, a mixture of carbon tetrachloride and argon was exposed for several hours to a silent electric dis-

charge. The argon did not enter into combination but was recovered without loss.

Other attempts to induce argon to enter into combination have been singularly successful. Berthelot, by means of the silent electric discharge, has effected the union of argon with benzene,<sup>39</sup> carbon disulphide,<sup>40</sup> and apparently with mercury. Berthelot describes the product formed by the union of argon with the elements of benzene, the first compound of argon produced in the laboratory, as consisting of "yellow resinous matter which, under the action of heat, decomposes, forming volatile products and leaving a bulky carbonaceous residue."

Troost and Ouward appear to have been able to effect the combination of argon with the vapor of magnesium by means of a powerful electric discharge.<sup>41</sup> Argon contained in a tube, furnished with magnesium wires connected with a Ruhmkorff's coil, was found to gradually diminish in volume under the influence of the discharge and finally to disappear, seemingly becoming united with the vapor of the magnesium. Under the same conditions platinum appeared to volatilize and combine with the argon in the same manner as the magnesium.

P. Villard has found that upon being compressed to 150 atmospheres, in presence of water, argon combines with the water to form a crystalline and dissociable hydrate, which is analogous to the hydrates of gases already known.<sup>42</sup> Almost as remarkable as the discovery itself is the failure on the part of chemists to detect argon previous to 1894. Cavendish isolated the gas, apparently obtained it in a pure state, and the account of his research has been in the hands of chemists for a hundred years. Simply because Cavendish inferred the relative freedom from impurities of his "phlogisticated air," from the smallness of the residuum he obtained, chemists were willing to leave the critical investigation of this residuum to the future until its explanation became necessary in clearing up other difficulties. It would be hard to find an example of a fallacy, arising from undue devotion to authority, more instructive than that of our mistaken views regarding the composition of the atmosphere previous to Lord Rayleigh's and Prof. Ramsay's brilliant discovery.

It is further interesting, in connection with the long delay in

detecting argon, to note the researches of Mallet, who, in 1870, published an account of an industrial method for preparing oxygen,<sup>1</sup> in which he unknowingly describes what could not fail to be the production of, if not pure, at least highly accumulated argon in connection with oxygen. Mallet's method consists in repeatedly pumping air into water, under high pressure, liberating the absorbed gases and again pumping them into water, repeating the process until the oxygen is sufficiently freed from other gases, for the use to which it is to be applied.

The isolation of the argon from the nitrogen would result, as Brauner has pointed out,<sup>17</sup> from the superior solubility of the former gas, the solubility of argon in water being to that of nitrogen in the ratio of 2.5 to 1. Repeating the process eight times produces a gas which, according to Mallet, consists of 97.3 per cent. of oxygen and 2.7 per cent. of nitrogen. That this so-called nitrogen is really nearly pure argon there can be little doubt; in fact, that the action of the process is, as here described, is proven by the fact that the curve representing graphically the decrease in the percentage of nitrogen after each operation shows that after the first few repetitions of the process the absorption coefficient of the so-called nitrogen which is gradually becoming richer in argon, approaches the coefficient of absorption of oxygen which is approximately the same as that of argon.

The failure to detect argon previous to 1894 is the more remarkable from the fact that the records of the progress of chemistry abound with accounts of atmospheric research. As Brunner has said "L'analyse chimique de l'atmosphère a été de tout temps une des parties de la chimie qui est attiré le plus l'attention des savants." A single periodical, the *Chemical News*, 1860-1896, describes about 200 investigations on air, and yet, notwithstanding the abundance of such researches, a careful survey of the literature on the subject since the time of Cavendish's classic experiments to those of Rayleigh fails to reveal even so much as a surmise that the air contained any gas which had not been isolated and studied.

It is not the author's intention to infer from this that the discovery of a gas, of the character of argon, had never been pre-

<sup>1</sup> *Ding. poly. J.*, 199, 112; *J. für Gasbereitung*, 1870, 538.

dicted, but merely to show that no such predictions has been made as a result of the study of the atmosphere.

There are two very remarkable instances of the anticipation of the discovery of argon. The first was that of Lieut. Col. Sedgwick, in 1890, and the second that of Boisbaudran shortly before the discovery of argon was announced.

Sedgwick, as a result of his study of the forms and relations of atoms, reached the conclusion that there must be an inactive element of the atomic weight commonly assigned to argon. He conceives atoms to be spheres with one or more flat places, the number of which correspond to the valence of the element. Sedgwick, on page 60 of his book "Force as an Entity," published in 1890, points out that an element whose atoms are perfect spheres, would be inactive and have an atomic weight of 20.

In his remarks on atomic weights<sup>1</sup> Boisbaudran gave a classification of the elements which led him to assume the existence of an unknown family of elements of atomic weights 20.0945,  $36.49 \pm 0.08$ ,  $84.01 \pm 0.02$ , and  $132.71 \pm 0.85$ . These elements, according to Boisbaudran, should be non-metallic, of even atomicity, the first two abundant in nature, and the member having the atomic weight 20.0945, which he now identifies with argon, should be more volatile than oxygen.

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## A RAPID METHOD FOR THE DETERMINATION OF SILICON IN SILICO-SPIEGEL AND FERRO-SILICON.

BY C. B. MURRAY AND G. P. MAURY.

Received January 27, 1897.

IN 1894 Furnace "A" at the Edgar Thomson Steel Works made the first silico-spiegel ever manufactured in this country. A determination of silicon and manganese was required in each cast, the silicon especially, as soon as possible.

The "aqua regia" method was the one tried. Various strengths of acid were used, but it was found almost impossible to get the metal into solution, even after passing the crushed "shot" through bolting-cloth. As high as 400 cc. aqua regia was used on one-half gram, the aqua regia being four parts nitric acid and three parts hydrochloric acid.

The fusion method, as recommended by Williams,<sup>1</sup> was also tried, but we were never able to make a determination in less than six to eight hours. The furnace made only a short run on silico-spiegel and for the time the matter was dropped. Last year we again made some silico-spiegel and were successful in finding a method for determining the silicon in a rapid and accurate manner and give the method in detail below.

*Preparation of the Sample.*—For the success of the method it is essential that the sample should be in a very fine state of subdivision. Grind in an agate or crush in a diamond mortar so that the sample will pass through a sieve made of bolting-cloth.

<sup>1</sup> *Trans. Am. Inst. Min. Eng.*, 17, 542.

**Operation.**—One-half gram of the sample is placed in a porcelain or platinum dish ; fifty cc. water, ten cc. hydrochloric acid (1.20 sp. gr.) and twelve cc. sulphuric acid (one part sulphuric acid, 1.84 sp. gr., to three parts water) are poured on it; heat until copious fumes of sulphuric acid are given off. Allow the dish to cool, so that there will be no spattering when taking up with acid. When cool, add about ten cc. hydrochloric acid, heat to soften the sulphate of iron, add about seventy-five cc. water, and bring to a boil. Discontinue the heating and note whether there is any effervescence when boiling ceases. If there is, the liquid must be evaporated until copious fumes of sulphuric acid are given off again, then taken up as before directed. Filter at once, wash thoroughly with hydrochloric acid (1 : 1) and hot water, ignite in a platinum crucible, and weigh. Add a few drops sulphuric acid and enough hydrofluoric acid to dissolve the silica. Evaporate to dryness, heat to decompose the sulphates, cool, and weigh. The difference in the two weights is silica, which can be calculated to silicon. The whole operation can be accomplished in thirty minutes.

The following are some results, both by our method and the fusion method :

No.	Our method.	Fusion method.
1	12.08	12.01
2	12.37	12.25
3	12.09	12.08
4	13.46	13.40
5	9.05	9.03

## A METHOD FOR THE COMPLETE ANALYSIS OF IRON ORES, WITH NOTES ON SÄRNSTRÖM'S METHOD OF DETERMINING MANGANESE.

BY GEORGE AUCHY.

Received January 25, 1897.

SÄRNSTRÖM'S method of determining manganese in iron ores, as described by Messrs. Mixer and DuBois, is to precipitate the iron in dilute hot solution by sodium carbonate, care being taken to add no more of this reagent than just enough to effect the precipitation of the iron ; then titrating (without filtering from the precipitated ferric oxide) with standard permanganate. The writer, in experimenting with Volhard's method,

and with Stone's modification of Volhard's method, had found that in working these methods it was necessary to add the zinc oxide in considerable excess of the amount necessary to completely precipitate the iron, for the reason that titration of the manganese in imperfectly neutralized solution gives too high results. But in Särnström's method we have, apparently, titration in incompletely neutralized solution without any tendency to high results as a consequence, as is shown by the accuracy in Messrs. Mixer and DuBois' work. It was thought by the writer that this apparent anomaly could perhaps be explained by the assumption that in Särnström's method manganese is carried down by the iron precipitate, as happens in Volhard's method, if certain precautions be not observed, and that this error compensates for the error of high results due to titration in incompletely neutralized solution. But the uniform excellence of the results given by Messrs. Mixer and DuBois operate against this view, and the following experiments made by the writer also seem to show that Särnström's method is free from these sources of error :

Manganese present. Per cent.	Manganese found. Per cent.	Number of cc. permanganate re- quired, theoretical.	Number of cc. permanganate re- quired, actual.
0.60	0.60	2	2.0
0.60	0.60	2	2.0
0.60	0.60	2	2.0
0.60	0.60	2	2.0
1.80	1.68	6	5.6
1.80	1.80	6	6.0
3.60	3.54	12	11.8
3.60	3.60	12	12.0
7.20	6.96	24	23.2
1.80	1.80	6	6.0
1.80	1.80	6	6.0
1.20	1.20	4	4.0
1.20	1.14	4	3.8
1.80	1.74	6	5.8
1.80	1.74	6	5.8
0.60	0.60	2	2.0
2.40	2.37	8	7.9
3.00	2.97	10	9.9
3.60	3.54	12	11.8
4.80	4.74	16	15.8
4.80	4.74	16	15.8

Manganese present. Per cent.	Manganese found. Per cent.	Number of cc. permanganate re- quired, theoretical.	Number of cc. permanganate re- quired, actual.
6.00	5.94	20	19.8
1.80	1.81	6	6.05
1.20	1.19	4	3.95
2.40	2.37	8	7.9
3.60	3.66	12	12.2
4.80	4.84	16	16.15
6.00	5.97	20	19.9
7.20	7.14	24	23.8

It would seem from these results that there is a tendency to slightly low results ; but that this is not due to manganese carried down with the iron precipitate seems shown by the fact that the same tendency exists when no iron is present. The following tests were made with manganese solutions free from iron, having exactly the same amounts of free acid present as in the previous experiments, and also using exactly the same amounts of sodium carbonate for neutralization.

Manganese present. Per cent.	Manganese found. Per cent.
0.60	0.60
0.60	0.60
0.60	0.57
1.20	1.20
2.40	2.37
3.60	3.54

There seems to be an entire absence of the tendency to high results existing in Volhard's method when titration is performed in incompletely neutralized solution. But further experiments led the writer to question whether, after all, he was right in his assumption that the titration in Särnström's method takes place in incompletely neutralized solution ; and the experiments following seem to indicate that the explanation of the mystery lies in the fact that in Särnström's method either the ferric oxide by its presence, in some way, prevents high results when solutions are incompletely neutralized, or the ferric oxide by its presence, in some way, prevents the precipitation of the manganese dioxide by titration, except the solution be thoroughly neutralized when titrated, the permanganate simply coloring the solution, and no manganese dioxide precipitating until more sodium carbonate is added. If the solution—incom-

pletely neutralized, but sufficiently so to precipitate the iron—be filtered from the precipitated ferric oxide before titration, the manganese in that case is not held up (if the solution be not too acid) but precipitates immediately upon the addition of the permanganate, and the result then becomes too high, as in Volhard's method, under similar conditions of neutralization.

Manganese present. Per cent.	Manganese found ; filtered from the ferric oxide be- fore titration. Per cent.	Manganese found ; filtered from the fer- ric oxide, but more sodium carbonate added before titration. Per cent.
3.60	3.66	3.60
3.60	3.63	3.60
3.60	3.66	....
3.60	3.75	....
3.60	3.75	....

It should be noted that when in the performance of the method by the regular way, the neutralization happens to be imperfect, and the permanganate therefore fails to throw down the manganese dioxide, and more sodium carbonate is consequently added, the result is apt to be too high if *much* more sodium carbonate is required, as appears from the following :

Manganese present. Per cent.	Manganese found. Per cent.
2.40	2.43
0.60	0.67
0.60	0.63

If little more sodium carbonate is required the result is not affected.

Manganese present. Per cent.	Manganese found. Per cent.
0.60	0.60
0.60	0.60
1.80	1.80
2.40	2.37
4.80	4.74
6.00	5.94
1.80	1.81
1.20	1.23

At all times an excess of sodium carbonate must of course be guarded against, but the exact point of neutralization can invariably and easily be obtained by performing the process as follows: Add seven grams of ammonium chloride; make the bulk of the solution 400 or 500 cc., add sodium carbonate *in the*

*cold* to a slight but permanent turbidity ; toward the last the sodium carbonate solution is added drop by drop from a burette; when a slight turbidity appears, which, if anything, increases by standing a minute but which shows no sign of a distinct precipitate, the reaction is complete (Herschel and Schwartzenberg). Bring to a boil with frequent stirring, which precipitates the iron completely ; then add one cc. more of sodium carbonate solution (one pound of crystallized salt to one liter of water), and titrate with permanganate. By performing the process in this way accurate results are invariably obtained. The ammonium chloride present makes the danger of manganese precipitating through an excess of sodium carbonate very remote, even if much more carbonate be added than directed. One-tenth cc. of permanganate (when the strength is 0.0056) should be deducted from the reading of the burette, as a performance in blank shows that that much permanganate is required to give a distinct color to a solution of that bulk.

The phenomenon noted in the examination of Volhard's method, that titration in nitric acid solution requires a deduction to be made in the result of 0.02 per cent.<sup>1</sup> also occurs in Särnström's method, as was shown by two experiments.

The Särnström method may be successfully used in steel analysis provided—as Messrs. Mixer and DuBois have said—that organic matter be first destroyed. But Stone's modification of Volhard's method is preferable, since in that method the organic matter does not interfere, being carried down with the ferric oxide and filtered off, and hence the time consumed in destroying the organic matter may be saved.

It is the writer's experience that the color method is, all things considered, as good as any for common use. But it is perhaps worth remarking that in the color method a standard *solution* is preferable to standard drillings, the time and labor of weighing out and dissolving the standard drillings for every analysis being thereby saved. In making up the standard manganese

<sup>1</sup> It is better to say that a deduction of 0.2 cc. permanganate (strength 0.0056) is required. With the weight of sample taken for analysis by Volhard's method this amounts to 0.02 per cent., as stated. But in Särnström's method only about one-third of this weight can be taken, and the deduction therefore would be 0.06 per cent. instead of 0.02 per cent. It would therefore have been better if in the article on Volhard's method the writer had directed a deduction of 0.2 cc. permanganate instead of a deduction of 0.02 per cent. in the result.

solution, the amount of nitric acid used for solution of the standard steel should, of course, be such that 100 cc. of the standard solution will contain as much acid as is used for solution of the steel to be tested. Ten cc. of the standard solution is in each case used, three cc. dilute nitric acid added, boiled with lead peroxide, etc.

#### A METHOD OF ANALYZING IRON ORE.

In making a complete analysis of iron ore it seemed an obvious application of Särnström's method to separate manganese, lime, and magnesia from iron by precipitating the iron as in that method, and filtering before titrating with permanganate. The writer had no access to Särnström's original article, but from the tone of the description of it given by Messrs. Mixer and DuBois, inferred that no such application is made by Särnström. In Crookes' Select Methods iron is separated from manganese in this way; also manganese from zinc; but there is no mention of lime and magnesia in this connection. Fresenius (old edition) gives a method by Herschel and Schwarzenberg for separating "iron sesquioxide from nickel, cobalt, zinc, manganese, and other strong bases" by neutralizing with ammonium carbonate in the cold in presence of much ammonium chloride, till the liquid loses its transparency, and does not clear up after a moment's standing, but, if anything, shows an increased cloudiness, without showing the least trace of a distinct precipitate; then bringing to a boil and boiling to expulsion of the carbon dioxide, and filtering from the completely precipitated basic iron oxide. But the writer was not sure that lime and magnesia were included in the term "strong bases;" and moreover, had much doubt as to the efficacy of the separation in the case of alumina. Experiments were therefore made on his own account, which showed that in carrying out the process, as already described in the first section of this article, namely, neutralization with sodium carbonate in the cold to slight but permanent turbidity, but with no trace of a distinct precipitate showing, then bringing to a boil, adding afterwards one cc. more of sodium carbonate solution, and filtering from the iron oxide, it occurs:

1. That in the absence of alumina all the zinc, manganese, and lime are found in the filtrate from the ferric oxide, but not



all the magnesia, which latter requires therefore a repetition of the operation for a complete separation from the iron.

2. That if seven grams of ammonium chloride be added to the solution before neutralization with sodium carbonate and precipitation of the iron, the separation of the magnesia, as well as that of the manganese, zinc, and lime, is, in that case, thorough and complete in one precipitation.

3. That if alumina be present, however (seven grams of ammonium chloride being also present), the alumina not only is not itself completely separated from the iron in one precipitation, but the small amount of alumina precipitating with the iron also carries with it a small amount of the magnesia or lime, or both (the test was made by adding phosphate and ammonium chloride to the concentrated filtrate from a basic acetate precipitation), and therefore two, and very often three precipitations are necessary to get the ferric oxide completely free from alumina, lime, and magnesia.<sup>1</sup>

4. That the presence of alumina in solution with the manganese, after filtration from the ferric oxide, interferes with the titration with permanganate, as the addition of the small quantity of sodium carbonate necessary to a thorough neutralization before titration, partially precipitates the alumina, and this keeps the manganese dioxide precipitate from balling together, thereby preventing any observation of the color of the liquid ; while if enough sodium carbonate be added to completely precipitate the alumina—although the titration can then be successfully performed—the result will be too low, the alumina apparently carrying down some of the manganese.

5. That if the alumina be precipitated by ammonia in slight excess, boiling off the excess, no manganese is carried down, and the manganese in the filtrate from the alumina may be conveniently and accurately determined by titration with permanganate.

With these facts ascertained, the scheme for analysis of iron ores would obviously be as follows :

<sup>1</sup> It should be noted, however, that the experiments on this point were made with a solution containing also titanous acid, equivalent to one per cent. ; so that it is probably the titanous acid which carries down the alumina. But as titanous acid in small amount is so frequently a constituent of iron ores, it was not thought necessary to investigate this point.

Take one-half gram of the ore for analysis. Dissolve and separate silica as usual. To the filtrate from the silica add two hornspoonsful (about seven grams) of ammonium chloride, and dilute to 275 cc. (or 300 cc. in rich ores). Add sodium carbonate solution (or the main part of the neutralization may conveniently be made with the solid carbonate<sup>1</sup>) from a burette, toward the last, after the solution turns from yellow to red in color, drop by drop, till the appearance of a faint cloudiness which persists on standing a minute, or even increases, without, however, showing any trace of a distinct precipitate.<sup>2</sup> Then bring to a boil with frequent stirring, the ferric oxide beginning to precipitate as soon as the heat is applied. Boil a few minutes. Add five drops more of sodium carbonate from the burette (about three-tenths cc., sodium carbonate solution of strength one pound crystallized salt to a liter of water) and stir. Allow to stand until the ferric oxide precipitate has completely settled. Filter and wash (not by decantation) with hot water.<sup>3</sup> The ferric oxide precipitate contains besides the titanous acid and phosphoric acid, also a small portion of the alumina, lime, and magnesia. Dissolve on the filter in hot hydrochloric acid, add the solution of the alumina later obtained, and precipitate with ammonia. Filter and weigh, and estimate alumina by difference. The filtrate from this precipitate—containing the small amount of magnesia or lime, or both, coming down with the iron in the first precipitation—is added to the main lime and magnesia solution after the latter has been freed from the manganese, as described later.

The filtrate from the first ferric oxide precipitate containing all the manganese, and all but a small part of the lime, alumina, and magnesia (and 0.01 or 0.02 per cent. of phosphoric acid if the phosphorus in the ore be extremely high, afterwards precipitated with the alumina) is brought to a boil and boiled a minute to expel traces of carbon dioxide (a very necessary pre-

<sup>1</sup> Ammonium carbonate, if free from organic matter, doubtless answers just as well, or probably better, as ammonium salts are desired in the solution, while sodium salts are of no use. But the writer prefers sodium carbonate on account of cheapness, and on account of being free from organic compounds, which interfere with the subsequent titration with permanganate.

<sup>2</sup> In observing the liquid, it is well to do so both by holding it between the light and the operator, and by reflected light. The cloudiness is best recognized, however, by working by reflected light.

<sup>3</sup> A nine cm. filter paper is hardly large enough, and either a size or two larger should be used, or else two nine cm. filters. After the first two washings the precipitate should be stirred up by the jet.

caution), ammonia added in slight excess, and the excess boiled off. The precipitated alumina, free from manganese, but carrying a little magnesia when much is present, is allowed to settle, filtered (by siphon preferably), and washed with hot water. Dissolve in hydrochloric acid and add to the ferric oxide solution. The filtrate from the alumina is brought to a boil and titrated with standard permanganate. Deduct from the reading of the burette the number of cc. of the permanganate taken up by the organic matter of the ammonium chloride used—previously ascertained by a trial in blank—and calculate the percentage of manganese. Add a small crystal or two of oxalic acid, and some hydrochloric acid to get the precipitated manganese again into solution (the manganese dioxide cannot be filtered off because it carries magnesia). Destroy the excess of oxalic acid by titrating with permanganate solution. Evaporate down and precipitate and filter the manganese (as sulphide) as directed in Blair's Chemical Analysis of Iron, and finish as usual—but determining the lime by titration with permanganate.

This method of analysis has the advantage over the basic acetate in that the precipitation of the iron takes place in small, instead of large, bulk of solution, with a consequent saving of time in evaporation; the separation from the manganese by the former process, moreover, being thorough and complete, while by the basic acetate, two basic acetate precipitations are necessary for a thoroughly accurate separation. If two basic acetate precipitations be made, the proposed method is very much quicker, but is also quicker if only one basic acetate be made. In the basic acetate method, no separate precipitation and filtration of the alumina is involved, but this precipitation and filtration requires considerably less time than is required to evaporate down the filtrate from the basic acetate precipitation to a workable bulk. Another advantage in the proposed method is in the determination of manganese by titration instead of by the rather tedious and troublesome gravimetric process. Still another is in the fact that the iron precipitate by the proposed method is one that shows no tendency to run through the filter, settles more rapidly, and is washed with much more ease than the basic acetate precipitate; moreover, this precipitation is simpler and more likely to be successfully performed by a beginner.

Following are some manganese results obtained in this way :

No.	Manganese present. Per cent.	Manganese found. Per cent.
1	3.60	3.60
2	3.60	3.60
3	3.60	3.60
4	3.60	3.60
5	3.60	3.60
6	3.60	3.54
7	3.60	3.60
8	3.60	3.36

The last result of the series is a poor one, some of the manganese evidently having precipitated with the alumina. This seemed a very singular circumstance in view of the fact that it is laid down by authorities that manganese is completely separated from alumina by precipitation of the latter with ammonia, and boiling off the excess ; all the writer's other experiments also went to prove the same thing. It was thought that perhaps the manganese had come down with the iron precipitate instead of with the alumina, but a careful examination of the iron precipitate showed no trace of manganese. Finally it occurred to the writer that a little carbon dioxide might have been in solution at the time of the alumina precipitation—it was remembered that the ammonia had been added before the liquid had been brought to a boil. To see whether in such an event manganese would precipitate a test was made by taking standard manganese solution, adding to it the amount of hydrochloric acid used in ore analysis, nearly neutralizing with sodium carbonate as usual, heating, but not to boiling, then adding the ammonia in slight excess, and bringing to a boil. Manganic oxide was seen to precipitate ; hence the necessity for the precaution already spoken of, of boiling the liquid before precipitating the alumina with ammonia.

That titration of the manganese solution, obtained in this way, by permanganate succeeds when no carbon dioxide is present, is shown by the following tests :

No.	Manganese present. Per cent.	Manganese found. Per cent.
1	3.00	3.03
2	1.20	1.19
3	1.80	1.80
4	2.40	2.40

If in the ore to be analyzed, zinc, nickel, and cobalt are to be tested for, the scheme of analysis just described must be modified as follows :

In the filtrate from the ferric oxide precipitate the alumina, manganese, nickel, cobalt, and zinc with ammonium sulphide, filter, dissolve in hydrochloric acid, filter from sulphides of nickel and cobalt remaining undissolved, and make a basic acetate separation in small bulk, and separate the zinc, nickel, cobalt, and manganese as usual, except that manganese is determined by titration, in solution made neutral by adding ammonia and boiling off the excess, instead of being determined as phosphate.

Another scheme of analysis by which alumina is directly estimated and iron is determined volumetrically in the same sample is to make *two* ferric oxide precipitations by neutralization with sodium carbonate as described, uniting the filtrates, precipitating, filtering, and weighing the alumina (if zinc, nickel, and cobalt are not to be tested for), which may afterwards be tested for iron ; titrating the filtrate from the alumina for manganese, etc. ; the ferric oxide precipitate being dissolved, reduced, and titrated for iron, no separate iron determination being made. But if this procedure be followed it is absolutely necessary to make a third ferric oxide precipitation as described, by way of precaution ; and if much titanous acid be present the writer is doubtful if even three precipitations will always free the ferric oxide entirely from alumina (and from magnesia or lime, or both, which comes down as long as the alumina does), although he has not, as yet, made any experiments on this point. In the table of manganese results, numbers 2 to 5, inclusive, were obtained in this way.

For the experiments on these methods a solution was used containing iron equivalent to forty per cent. ; alumina equivalent to ten per cent. ; manganese 3.60 per cent. ; lime fifteen per cent. ; magnesia fifteen per cent. ; phosphoric acid two per cent. ; titanous acid one per cent. These experiments need not be given in detail.

Further experimenting—which the writer at present has not the opportunity to perform—is intended. For instance, in the first method of separation described—precipitation of the iron by

neutralization with sodium carbonate, followed by a second precipitation of the iron (and alumina) by ammonia—when zinc, nickel, and cobalt are present, experiment might perhaps prove it feasible to completely precipitate these metals as sulphides by hydrogen sulphide in the filtrate from the first ferric oxide precipitate; afterwards precipitating the alumina by ammonia and determining the manganese by titration as directed in the scheme for analysis when no zinc, nickel, and cobalt are present. Nickel and cobalt could undoubtedly be completely precipitated in this way, and the writer has hopes that the zinc, also, would be completely thrown down from the dilute, nearly neutral solution. At least by the aid of sodium dithionate, the zinc would be completely precipitated.<sup>1</sup> In that case, this method of separation would be simpler and more convenient than the one suggested. In the method suggested it would perhaps be better to separate the zinc, nickel, and cobalt from the alumina by ammonia and ammonium chloride instead of by a basic acetate precipitation.

No experiments have been made by the writer regarding the accuracy of the separation of the magnesia from the iron and alumina by these two precipitations described in the first method (precipitation by neutralization with sodium carbonate, followed by precipitation by ammonia). It was not thought necessary to experiment on this point, because authorities unite in considering the separation of iron and alumina from lime and magnesia by a precipitation of the former by ammonia to be sufficiently accurate—one precipitation being considered by Blair sufficient to separate all the lime and magnesia from the iron and alumina; in this method two are used—only one by ammonia, but the first precipitation, by neutralization, in all probability separates nearly as large a proportion of the magnesia as a precipitation by ammonia would do, and quite as large a proportion of it as a basic acetate precipitation would effect. But it is considered that the basic acetate separation of magnesia from iron and alumina is rather better than the separation by ammonia; and if desired, the second ferric oxide precipitation of the method suggested may of course be made by basic acetate. But in this event it is the writer's opinion that the precipitation may be made in much less

<sup>1</sup> J. Ribon : *Bull. Soc. Chim.*, 50, 518.

bulk (say 400 cc.) to separate the iron and alumina from the trifling amount of magnesia remaining from the first separation by neutralization, than is ordinarily required.

A quicker way of performing the first method than the one described (zinc, nickel, and cobalt being absent) would be to precipitate the aluminum and manganese by ammonium sulphide in the filtrate from the first ferric oxide precipitate; then filtering, dissolving in hydrochloric acid, separating alumina by precipitating with ammonia, boiling off excess; titrating the filtrate for manganese; filtering off the precipitated manganese dioxide; and adding filtrate to the main lime and magnesia solution (which has meanwhile been evaporated down) to recover the lime and magnesia (if any) carried down by the ammonium sulphide precipitation of the alumina and manganese. But, as before stated, the manganese dioxide precipitate carries down magnesia; but doubtless not when the magnesia present is small in amount as would be the case here. This point also, however, must be tested by experiment.

The Särnström reaction may evidently also be made use of in zinc ores for separating iron, alumina, and manganese from zinc, previous to titration of the latter with ferrocyanide. The method at present most in use, at least in the West, seems to be that of von Schulz and Low. But Mr. Bertrand Hinman finds their method inapplicable to eastern ores (on account of the insolubility of these ores, and also on account of the higher percentage of iron which makes the separation from zinc by ammonia and ammonium chloride an incomplete one) except certain modifications be adopted. Mr. George C. Stone, however, finds that even with these modifications the method does not work with New Jersey ores, and originates another method in which the iron and aluminum are separated from the manganese and zinc by precipitation with barium carbonate; and the latter titrated with ferrocyanide, manganese being determined in a separate portion, and the zinc then estimated by difference. Very accurate results are obtained by this method, but it would be just as accurate and convenient to apply Särnström's method as follows: Obtain the ore in hydrochloric acid solution. If not enough iron be present add ferric chloride solution in sufficient

<sup>1</sup> This Journal, 17, 473.



amount. Add about seven grams ammonium chloride; dilute to 300 cc.; neutralize in the cold with sodium carbonate till the liquid loses its transparency as previously described; bring to a boil and boil a minute; add one cc. sodium carbonate solution and mix; titrate for manganese with permanganate; filter from the mixed iron and manganese precipitate (according to Crookes, page 200, no zinc comes down with the manganese dioxide precipitated in this way) and wash with hot water; and titrate the filtrate with ferrocyanide for zinc. Instead of filtering and washing the mixed ferric oxide and manganese dioxide precipitate, however, it would be better to dilute to a definite volume, and, after mixing, decant through a filter an aliquot portion.

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The writer takes this opportunity to make a few additional remarks on the determination of phosphorus in steel and cast iron. In a recent paper on that subject he advocated the use of double filters of Schleicher and Shüll's No. 579 or 589 black ribbon for the filtration of the yellow phosphomolybdate precipitate by aid of the pump, using the same filters for a number of different filtrations in succession. To this suggestion he wishes to add that these filters can very well be also used again the following day, or after having been dried out, for the same purpose; but that, for such an extended use, the number 589 black ribbon answers better than No. 579. The filters should not be unfolded when placed away for another use.

In filtering from the undissolved zinc through cotton wool, as in the method described in the article referred to, the same cotton wool may be made to answer for two consecutive filtrations, provided the percentage of phosphorus in the second of the two be not too low (under 0.05 per cent.). Below 0.05 per cent., fresh cotton should be used so as to get as rapid a filtration as possible. Several uses of the same filter clogs it considerably. Instead of performing this filtration by the pump, it is more convenient, owing to the extreme quickness and facility with which the liquid is drawn through the cotton wool, to use the mouth, by means of a clean rubber tubing of convenient length connected with the filtering flask.

Twenty-five cc. sulphuric acid (two of water to one of acid) was suggested for acidification of the phosphorus solution pre-



vious to the addition of a mustard-spoonful of zinc. If with the zinc in use it is found that this amount of acid dissolves it too quickly, or not quickly enough, the proper amount of acid to be used is found by varying the quantity added by one or two-tenths cc. If, for instance, twenty-five cc. are found to dissolve the zinc too quickly, so that the color of the reduced solution is only wine colored instead of green, as it should be, then 24.9 cc. will usually be found the right quantity for use on every occasion. It should perhaps be pointed out to those who have never used the Emmerton process that in titrating the reduced solution, the end point of the titration does not for some reason manifest itself with such suddenness as in the reductor process, and care must therefore be taken to note that the pink coloration is a distinct and permanent one.

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[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CINCINNATI.]

## LI. THE USE OF ALUMINUM FOR CONDENSERS.

BY T. H. NORTON.

Received January 18, 1897.

IN connection with the extended use of aluminum in this laboratory for various forms of apparatus, water-baths, air-baths, Bunsen burners, hot water filtering funnels, etc., it seemed desirable to study the availability of the metal for condensation processes.

For this purpose a condenser was constructed as follows: The outer jacket was of glass; the inner tube was of aluminum and possessed the following dimensions: length, 122 cm., external diameter, one cm., inner diameter, eight and one-half mm., weight per meter, twenty-nine grams. At a distance of fifteen cm. from the end, the tube was bent at right angles. This permitted of connection with a distilling flask, without allowing the condensing vapors to come in contact with any substance but aluminum. It might be mentioned here that in order to bend an aluminum tube of these dimensions satisfactorily, it is necessary to fill it with molten lead, and further, that several distillations with water are requisite in order to remove completely slight traces of lead adherent to the surface of the aluminum, after this operation.

The method of testing the condenser was to distil a measured

<sup>1</sup> Read before the American Chemical Society at the Springfield Meeting.

quantity of a liquid from the glass flask, used as a still, collect the distillate in glass, evaporate it from weighed platinum dishes and note the weight of the ignited residue, thus ascertaining whether there was any appreciable attack on the aluminum. Nothing was attempted beyond the ordinary precautions for preventing dust from contaminating the distillates.

The liquids first employed were organic. In each case 500 cc. were distilled, and the weights of the residue left on evaporating the distillate noted. The following results were obtained:

Liquid.	Residue from 500 cc.
Ethyl alcohol (specific gravity 0.809).....	0.001 gram.
Benzene .....	0.0016 "
Nitrobenzene.....	0.0004 "
Chloroform .....	0.0002 "
Ethyl ether .....	0.0000 "
Acetone .....	0.0001 "

In all these cases it was evident that very rapid distillation could be carried on with an exceedingly short tube, on account of the high conductive power of the aluminum. The residues obtained showed that there was practically no attack upon the aluminum.

The deportment of the metal towards steam was next studied, and here it was deemed wise to establish in all cases comparative experiments with glass and block tin. The glass condenser tube used for this purpose was eighty-four cm. long and had an inner diameter of sixteen mm.; the tin condenser tube was 305 cm. long and had an inner diameter of twenty-one mm. With the exception of differences in the superficial surface for condensation, other conditions were essentially identical. Three series of distillations were carried on with the three following samples of water :

- A. Hydrant water (Ohio River water), containing much impurity.
- B. " " " " " " less "
- C. Distilled water.

In all cases 500 cc. were employed. The following residues were obtained :

	Aluminum.	Block tin.	Glass.
A.....	0.0112	0.006	0.0118 gram.
B.....	0.0032	0.0028	0.0091 "
C.....	0.0035	0.005	0.008 "

A check determination on the amount of dust collecting in the platinum dish during the time for evaporation, showed it to be 0.0002 gram after ignition.

These results would show that as far as purity of the product is concerned, aluminum possesses about the same advantages over glass as tin, in connection with the distillation of water. In lightness and conductivity it exhibits marked superiority to the tin.

For use with neutral organic liquids it is well adapted, more especially in the distillation of low boiling substances such as ether. Here also the high thermal conductivity, as well as the absence of brittleness, are factors in its favor as compared with glass.

Mr. R. W. Hochstetter rendered valuable assistance in the determination of the above data.

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[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CINCINNATI.]

## LII. ON THE VOLATILITY OF CERTAIN INORGANIC SALTS.

BY T. H. NORTON AND D. M. ROTH.

Received January 18, 1897.

IN connection with some experiments on the volatility of sodium borate and sodium fluoride, carried on in this laboratory, it was thought advisable to make use of the method employed for certain salts by Bunsen nearly thirty years ago, but, as far as we can find from the literature, not used since then. This method consists in noting the time required for the volatilization of 0.01 gram of the substance under examination, in the form of a bead in a loop at the end of a platinum wire, after introduction into the hottest part of the Bunsen flame.<sup>1</sup> The disappearance of color when the substance is completely volatilized is marked and sudden. Naturally, great care must be observed in assuring, for purposes of comparison, identical conditions of location in the flame, temperature of the flame, etc. The method is of course applicable to such compounds only as impart color to the flame. Following Bunsen's example, the time required for the volatilization of 0.01 gram of sodium chloride was taken as unity. In this connection the volatility of most of the

<sup>1</sup> *Ann. Chem.* (Liebig), 138, 263.

salts studied by Bunsen was redetermined and the following additional salts were examined for the first time: Borax, sodium fluoride, potassium fluoride, and barium chloride. The results of all determinations are tabulated below. Bunsen's published figures are given in a separate column. Slight variations from his results are to be noticed in most cases. The material employed was the purest obtainable. Duplicate determinations always gave concordant results:

Salt.	Seconds.	Time of volatilization of 0.01 gram. Sodium chloride as unity.	
		N. and R.	Bunsen.
Sodium chloride.....	13	1.00	1.00
Sodium sulphate.....	130	10.00	15.04
Lithium carbonate.....	130	10.00	8.74
Potassium sulphate .....	87.5	6.73	7.89
Sodium carbonate.....	95.5	7.38	7.50
Potassium carbonate ....	47	3.61	3.23
“ chloride.....	12	0.923	0.776
“ bromide.....	7	0.538	0.487
“ iodide .....	5.5	0.423	0.352
Sodium borate .....	215.5	16.54	....
“ fluoride .....	104.5	8.04	....
Potassium fluoride .....	39.5	3.04	....
Barium chloride.....	1560.0	120.00	....

Tests were also made with calcium chloride, strontium chloride, and magnesium chloride. All three underwent decomposition, leaving a non-volatile, alkaline residue. Calcium sulphate and calcium fluoride were likewise tested. In both cases, although a slight coloration was imparted to the flame, there was no loss of material capable of detection by the balance.

## COLOR REACTIONS OF NITRIC AND CHLORIC ACIDS WITH CERTAIN AROMATIC BODIES.<sup>1</sup>

BY E. C. WOODRUFF.

Received January 8, 1897.

THE object of this research was to find some new practical tests for nitric and chloric acids, more especially tests that would differentiate the two both in mixtures and separately. The latter object has been attained several times over. The former is more difficult for several reasons. In general, chloric

<sup>1</sup> A thesis presented for the degree of Master of Science to the Council of the Graduate School of the University of Michigan, June, 1896. Communicated by O. C. Johnson.

acid produces a darker color reaction than nitric, in some few cases sufficiently so as to indicate chlorates in the presence of nitrates, in almost all cases enough darker to completely mask the nitrate effect. In some cases the effects are indistinguishable. Still two methods will be given later whereby the nitrate effect can be made to predominate, and best of all, one test has been found that, properly manipulated, accomplishes the desired result very well.

#### THE DIMETHYL ANILIN TEST.

The general method of procedure was as follows : About one cc. of the test solution, generally a solution of two grams of the aromatic substance in 100 cc. of concentrated sulphuric acid, was placed in a dry and clean test-tube and one drop of the nitrate, chlorate, or other inorganic salt solution was added. The whole was agitated and set aside until cold and the color fully developed. Thereupon a slight excess of a strong solution of potassium hydroxide or ammonium hydroxide was very slowly added, and, after standing a little while, enough water was added to redissolve any precipitate that might have formed, if it proved to be soluble. The color was noted at three stages, before and after neutralization, and after dilution. Generally the dilution did not weaken the color, as in most cases the precipitate was coloring matter in contact with a saturated solution of the same.

The organic substances selected for the tests are fairly typical of the main groups of the aromatic series. At least of those groups that present color reactions, *i. e.*, those bodies containing hydroxyl groups, or amido groups, or both. The following is a classified list :

#### PHENOLS :

*Monoxybenzene* : Phenol,  $C_6H_5.OH$ .

*Dioxybenzene* :  $C_6H_4.(OH)_2$ .

Pyrocatechol, (1 : 2) ;      Resorcinol, (1 : 3) ;

Hydroquinone, (1 : 4).

*Trioxybenzene* :  $C_6H_3.(OH)_3$ .

Pyrogallol, (1 : 2 : 3).

## CRESOLS :

*Monoxyluene* :  $C_6H_5.CH_3.OH$ .*Dioxyluene* :  $C_6H_4.(OH)_2$ .*m*-Cresol, (1 : 3).

Orcinol, (1 : 3 : 5).

## OXYACIDS :

*Monobenzoic acid* :  $C_6H_5.OH.CO_2H$ .*Triobenzoic acid* :  $C_6H_2.(OH)_3.CO_2H$ .Salicylic acid, (1 : 2). Gallic acid, (1 : 3 : 4 : 5— $CO_2H$  in 1). $\alpha$ -NAPHTHOL,  $C_{10}H_7.OH$ .ALIZARIN, Dioxyanthroquinone, (1 : 2).  $C_{14}H_9.(CO)_2.C_6H_4.(OH)_2$ .

## AMINES :

*Amidobenzenes* :Anilin,  $C_6H_5.NH_2$ . Dimethylanilin,  $C_6H_5.N(CH_3)_2$ .Acetanilid,  $C_6H_5.NH.CO.CH_3$ .Diphenylamin,  $(C_6H_5)_2.NH$ .*Amidotoluenes* :  $C_6H_4.CH_3.NH_2$ .

Orthotoluidin, (1 : 2). Paratoluidin, (1 : 4)

*Amidophenols* :Diamidophenol;  $C_6H_3.(NH_2)_2.OH$ .Paramidometacresol, or "metol"  $C_6H_3.CH_3.OH.NH_2$ . $\alpha$ -NAPHTHYLAMIN,  $C_{10}H_7.NH_2$ .

Table No. 1 gives in condensed tabulated form the reactions of these test solutions potassium nitrate, potassium chlorate, potassium bromate, potassium iodate, potassium bromide, potassium iodide, and a mixture of potassium chloride and nitrate. The colors are indicated thus :

V-violet; I-indigo; Bl-blue; Gr-green; Y-yellow; O-orange; R-red; W-white; Gra-gray; Br-brown; Pur-purple; Car-carmin; Cri-crimson; Pk-pink; Ch-cherry; Blo-blood red; YBr-yellowish brown; etc.

The modifying adjectives are indicated thus :

s-strong; l-light; d-dark; v-very; m-muddy.

This gives a means of expressing nearly 300 reactions on one page.

In making out this table the general method of experimentation as given on page 157 was followed. The phenol solution was of thirty per cent. strength. It was made from crystals that had somewhat reddened. Still it gave a perfectly white solution

that at the end of one month showed not the slightest discoloration. It is one of the strongly recommended tests for nitrates, not being interfered with by bromides nor iodides nor any of the metals if the proper alkali be chosen for neutralization. The same can be said of the salicylic acid test. The solution consisted of one gram of sodium salicylate dissolved in forty cc. of concentrated sulphuric acid. These two tests depend on the formation of ammonium or potassium picrate, giving a solution of a strong yellow or greenish yellow color. Another method of performing the phenol test deserves mention. It is probably more delicate though not so quick-acting as the one first given. The final result is the same. Into a dry test-tube is put one cc. of concentrated sulphuric acid. On this is very carefully floated a layer of a saturated water solution of phenol, not more than one-half cc. Now a drop of the unknown is allowed to fall gently on the upper layer, generally immediately producing a strong brown ring. After standing for some time the whole is shaken and neutralized, when a strongly picrate-colored solution indicates a nitrate. Chlorates give a brownish yellow instead of a greenish yellow. This serves as a distinguishing test in solutions where only one of the two is present.

The di- and trioxybenzenes furnish still more delicate tests for both nitrates and chlorates, but unfortunately give the same result with both as far as color is concerned, though perhaps a somewhat stronger effect with chlorates. Hydroquinone is the best of the four by far, giving a clear white solution possessing comparatively remarkable keeping qualities. A three per cent. solution was used. The resorcinol keeps well but gives a light brown solution, making it unsuitable for delicate tests unless freshly prepared. The pyrocatechol and the pyrogallol solutions do not keep at all if allowed access to the air. In these cases the test was performed by adding a minute crystal of the pyrogallol or the pyrocatechol to one cc. of sulphuric acid already in the test-tube, and going through the operations somewhat rapidly. The resorcinol used was two per cent. strong. All four under the proper conditions give the same result, a yellow solution with either a brown or a green tinge.

The monoxytoluenes give practically the same result as the phenols, both as regards delicacy and certainty of result, and,

although the test solution itself is somewhat brownish, still the effect of this on the final color is absolutely nothing at all, which cannot be said concerning any color in the test solutions where mere oxidation and not nitration is concerned.

The strength of the orcinol solution was two per cent. It was light brown in color but kept well and gave good results. Its special value was in the different results it gave while still acid with nitrates and chlorates, strong yellow red with the former and strong green with the latter.

The gallic acid solution, one per cent., was a disappointment. Although it gave a clear white test solution, and strong color reactions, with the nitrates especially, still it would give some color with bromides and iodides, and sometimes on neutralization without having any other salt added to it.

Naphthol and naphthylamin, both one per cent., gave strong clear tests. The naphthylamin distinguishes nitrates and chlorates as per table.

The alizarin was a bleaching test. Alizarin was added to sulphuric acid until a pink or light crimson solution was obtained. This, plus water, would give a bright yellow, plus potassium hydroxide, would give a strong purple, but nitrates, chlorates, bromates, iodates, and iodides so affect the sulphuric acid solution that addition of potassium hydroxide gives a colorless, or at the most, a very light purple result.

Acetanilid, one per cent, is sufficiently explained by the table.

Diphenylamin, four per cent., gave a light green solution which gradually darkened. This makes a fairly delicate test for nitrates, but there are several serious faults in its workings. First, it gives a rather poorly keeping solution. Second, it will not bear dilution or neutralization, so as to eliminate the effects of bromides and iodides, and so as to distinguish between nitrates and chlorates, even when only one of the two is present, nitrates, chlorates, bromates, and iodates all giving practically the same color. Third, it must be kept cool; heat alone, even the heat generated by adding a drop of distilled water to two or three of the solution may give the color supposedly due to a nitrate. Heating changes it first to green, then to a blue, and finally to dense black flakes in a colorless liquid in which water no longer produces a muddy brown precipitate as before.



The anilins and the toluidins will be treated later, after the comparative indices.

"Amidol," or diamidophenol hydrochloride, one per cent., makes a very delicate quick-acting test in acid solution, the test solution keeping very well considering its susceptibility to atmospheric oxidation. This latter sensitiveness somewhat spoils the effect of neutralization unless the test is performed rapidly.

"Metol," or paramidometacresol, one per cent., makes a test solution that resembles hydroquinone in its keeping properties and reactions.

Table No. 2 gives a comparative index for nitrates, and Table No. 3 a similar index for chlorates. These indices are arranged as follows: The first column contains the list of test solutions with its own colors marked. Of the remaining columns those to the left of the central double line contain the reactions on neutralization with potassium hydroxide, and those to the right on neutralizing with ammonium hydroxide. Fifteen drops of the test solution and one drop of a five per cent. solution of the nitrate or chlorate gave reaction (1); six drops of water gave reaction (2); an insufficient quantity of the neutralizing agent, reaction (3); an excess of the same, reaction (4); lastly, equal dilution with water, reaction (5). The remaining columns indicate the comparative strength of the color produced after the reaction whose number occurs at the top. A indicates the strongest color, B the next strongest, and so on. In each case the comparison is made only with the other colors in the same column. The fact that any one reaction is marked A means only that it gave the darkest color, not that it gave the clearest, most distinctive, or even most delicate test. The addition of water in the second reaction was for the purpose of preventing the intense heating effect produced by dropping strong potassium hydroxide solution into concentrated sulphuric acid. In some cases this modified to a considerable extent the reaction as given in the General Table. Further important details will appear on examining the indices. Especially significant is the fact that the strongest tests for nitrates were not always the strongest for chlorates even when they gave the same color, and vice versa.

By far the most interesting and most valuable results came from the study of the anilins and the toluidins. Table No. 4 shows the reactions of ten combinations of these substances, both as to the actual color produced and the comparative strength of the colors at different stages. A great many peculiar features came out in this series. The green and blue effects in the chlorate series gradually faded away leaving brown. A little water might restore the color which would soon again fade away. Again addition of water might reproduce the color which would more slowly disappear. Finally, considerable dilution would restore the color so that it would fade quite slowly but permanently. The green and blue effects to which reference are made are the ones in the column headed  $\text{H}_2\text{O}^{(4)}$ . Effects of the same nature, but during the process of neutralization, were noticed in the experiments with mixtures of potassium nitrate, with potassium chloride or potassium chlorate, as per table. In all cases where orthotoluidin was used a strong green appeared while adding potassium hydroxide. Sometimes it persisted for quite a while after complete neutralization. All traces of green eventually disappearing, addition of water reproduced the color which faded and was again reproduced as above.

The tests to which particular attention is called are those in horizontal lines (8) and (9). Notice the difference in the first effect in all four cases. Test No. (9), it will be noticed, gives the much desired means of detecting a nitrate in the presence of chlorates, bromates, and iodates. The first operation is the important one. If the chlorate be not in too great excess the blood red color produced by the nitrate is sure to show. Below are given some data on the sensitiveness of this test. It will be noticed that though chlorides alone have no color effect, they very much intensify the nitrate effect. The best formula appeared to be :

Dimethyl anilin .....	2 drops.
Paratoluidine.....	0.2 grams.
Sulphuric acid .....	10 cc.

It gives a colorless solution that keeps well.

On the same page are given data on the sensitiveness of the phenol, salicylic acid, and hydroquinone tests for nitrates, and

the anilin test for chlorates. A remarkable feature about the last is the radical change in color on standing.

Two methods of removing or reducing the strength of chlorates in a solution containing nitrates have been experimented with.

(1). Acidify with sulphuric, add hydrochloric, and boil until on adding another drop of hydrochloric and boiling no yellow color appears. Now the phenol test can show the nitrate without the slightest trace of the brown color due to chlorates.

(2). Carefully evaporate just to dryness, add cold water not sufficient to redissolve all the chlorate, dilute, and use the dimethylanilin test. All the nitrate dissolves before an equal quantity of chlorate, and as the test is good for nitrates in the presence of the same bulk of chlorates, it will work even more surely with a less amount.

An actual experiment of this sort ran as follows: Twenty cc. of water was saturated with potassium chlorate at about 50° C. and one gram of potassium nitrate added. When the solution had cooled to the temperature of the room, some of the potassium chlorate had crystallized out. Still more potassium chlorate than nitrate remained in solution. One drop of this gave a dark brown test with traces of crimson. The chlorate masked the nitrate. But when some of the solution was diluted with four volumes of water, in spite of the fact that the chlorate exceeded the nitrate in the same ratio as before, one drop gave a strong crimson reaction, the chlorate effect being overlooked. Then the original solution was evaporated to dryness, the residue cooled, and agitated with ten cc. of cold water. Now a test showed strong crimson but with a brownish tint. On adding four volumes of water to some of this solution the brown tint did not appear, only the crimson nitrate effect.

The dimethylanilin test has proved to be practically an absolute test for nitrates. The test has been successfully worked in the presence of each of the inorganic salts commonly met with, even the most powerful oxidizing and reducing agents. Of the metals, Sn<sup>II</sup>, Sb<sup>III</sup>, Fe<sup>II</sup> are the only ones that tend to spoil the test by reducing the nitrate. Oxalic, acetic, hydrosulphuric, iodic, and arsenious acids seemed to exert a similar influence on the test. However, the only one of these two lists that was

always deleterious was  $\text{Fe}^{2+}$ .  $\text{K}_4\text{Fe}(\text{CN})_6$ ,  $\text{K}_3\text{Fe}(\text{CN})_6$ , and  $\text{KNO}_3$ , seemed to give a pink to crimson color that might have been due to impurities in the reagents. Addition of nitrate, however, immediately strengthened the color to such an extent as to obviate any difficulty on that score. The color produced by potassium ferrocyanide was very feeble, which result seemed to uphold the suspicion of impurity in the other cases. Potassium chloride, potassium bromide, potassium iodide, chlorine, bromine, iodine, and potassium thiocyanate seemed to have no effect whatever, excepting that potassium chloride strengthened the nitrate reaction. Similarly potassium chromate, potassium dichromate, potassium arsenate, and potassium permanganate presented no color reaction of their own, but seemed to help the nitrate in its reaction. Potassium permanganate lost its own color when added separately to the test solution. As mentioned above, potassium chlorate, bromate, and iodate do not interfere with the test under ordinary circumstances.

In view of these various results, to get the maximum efficiency out of the test, would require the following method of procedure :

To the unknown add potassium chlorate, if not already present, then some hydrochloric acid, and boil. This will oxidize all the reducing agents that might otherwise be harmful, without introducing enough excess of potassium chlorate to injure the result.

## TABLE NO. I. GENERAL INDEX OF REACTIONS.

Test solution of	KNO <sub>3</sub> .	KOH.	KClO <sub>3</sub> .	KOH.	KBrO <sub>3</sub> .	KOH.	KIO <sub>3</sub> .	KOH.	KBr.	KOH.	KI.	KOH.	KCl and KNO <sub>3</sub> .
Phenol.....	Y	sGrY	RY	dGrBr	KOH. RY	1YBr	sRY	1YBr	1Y	W	Md	W	Y GrY
Pyrocatechol.....													
Resorcinol.....	Y	Y	BrY	1Br	BrY	1Br	MdBr	1Br	1Y	W	Md	W	Y Y
Hydroquinone. . .	sYR	YR	YBr	YBr	YBr	YBr	MdBr	YBr	W	W	MdGra	W	YBr YBr
Pyrogallol.....	sYR	sYBr	vdBr	vlBr	YBr	1Br	sBr	1Br	1Y	W	Md	W	sYR YR
Cresol.....	Y	sY	BrY	dGrBr	BrY	vsRBr	MdBrY	vsRBr	Y	vl	Md	vl	Y sY
Orcinol.....	sYR	sYR	sGr	YBr	sGr	Br	dMd	sBr	W	W	Md	W	sYR sY
Salicylic acid.....	1Y	sY	dYBr	sBr	RY	sBr	RY	sBr	1Y	W	Md	W	1Y sY
Gallic acid.....	sYR	sYBr	Y	1Y	Y	W	MdGr	1Y	W	1PkBr	Md	1PkBr	RY Y
α-Naphthol.....	sBrY	sY	sBrY	Br	sKY	Br	MdGr	Y	W	W	Md	W	sBrY Y
Alizarin.....	Y	W	Y	W	BrY	W	Y	W	Y	Pur	Md	W	Y W
Anilin oil.....	dRBr	Y	vsBl	sPur	dBl	1Br	sRBr	1Br	RY	W	Md	W	sPurBr Br
Dimethylanilin...	RY	sY	Y	vlBr	Y	vlBr	sRY	vlBr	Y	W	Md	W	sRY sY
Acetanilid.....	1Y	sY	dRBr	dGrBr	YBr	Br	YBr	1Br	RY	W	Md	W	1Y Y
Diphenylamin...	sBl	Y	sBl	PurBl	sBl	1Br	sBl	sBl	sGr	W	Md	W	sBl
Orthotoluidin...	sYBr		sBl		sBl	1Br	MdsBl	1Br	YBr	W	Md	W	sBrPur GrY
Paratoluidin.....	vdBr	Br	vsBr	Br									
"Amidol".....	vsYR	YBr	sPurR	YGr	sR	YGr	vsPurR	YBr	Y	1Br	Md	1Br	RY YBr
"Metol".....	YR	YBr	Y	YBr	YR	Y	sYR	sYBr	vlY	W	Md	W	Y YBr
α-Naphthylamin. . dPurGr		Y	dYR	dBr	dYR	dBr	MdBr	YBr	W	W	Md	W	dPurR RY

TABLE NO. 2. COMPARATIVE INDEX FOR NITRIC ACID.

Test solution of	(1) KNO <sub>3</sub>	(2) H <sub>2</sub> O	(3) KOH	(4) KOH	(5) H <sub>2</sub> O	(6) KNO <sub>3</sub>	(7) H <sub>2</sub> O	(8) NH <sub>4</sub> OH	(9) NH <sub>4</sub> OH	(10) H <sub>2</sub> O	(11) H <sub>2</sub> O	(12) H <sub>2</sub> O	(13) H <sub>2</sub> O	(14) H <sub>2</sub> O	(15) H <sub>2</sub> O
Phenol, W.....	Y	1Y	1Y	1Y	1Y	1Y	1Y	1Y	1Y	1Y	1Y	1Y	1Y	1Y	1Y
Protocatechol .....	Y	Y	O	sY	sY	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y
.....	Y	RY	dBrR	vdBr	vsYBr	vdBr	sRBr	dRBr	vsRBr	sYBr	vsRBr	sYBr	vsRBr	sYBr	vsRBr
.....	BrY	1Y	dBr	vdBr	sBr	vdBr	vdBr	vdBr	vsBr	vdBr	vsBr	vdBr	vsBr	vdBr	vsBr
Cresol .....	dRY	O	dYR	dRY	sBrY	dRY	YBr	O	sRBr	sYBr	sRBr	sYBr	sRBr	sYBr	sRBr
Orcinol, lBr .....	1Y	1Y	1Y	sY	sY	1Y	W	sY	sY	sY	sY	sY	sY	sY	sY
Salicylic acid, W.....	vsBr	dYBr	Br	vdBrR	sBrY	vdBr	vdBr	dBr	sYBr	sYBr	sYBr	sYBr	sYBr	sYBr	sYBr
Gallie acid, vly.....	sGrBr	O	1Y	dRY	sO	sGrY	YBr	Y	sRBr	sYBr	sRBr	sYBr	sRBr	sYBr	sRBr
a-Naphthol, lBr .....	1Y	1Y	1Y	1Y	1Y	1Y	1Y	1Y	1Y	1Y	1Y	1Y	1Y	1Y	1Y
Alizarin, sPk.....	vdBrR	Gr	1YBr	MdBr	Y	vdBr	sBlGr	MdY	MdY	MdY	MdY	MdY	MdY	MdY	MdY
.....	Y	Y	Y	sY	sY	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y
.....	Gr	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y
.....	Br	vdBr	MdBr	MdBr	Y	vdBr	sYBr	GrY	GrY	GrY	GrY	GrY	GrY	GrY	GrY
Paratoluidin .....	vdBrR	dBr	vdBrR	vdBrR	vsR	vdR	vsBr	vdBr	vsBr	vdBr	vsBr	vdBr	vsBr	vdBr	vsBr
"Amidol," vly.....	Y	BrY	O	sYR	sYBr	Y	10	RBr	vsBr	vsBr	vsBr	vsBr	vsBr	vsBr	vsBr
"Metol," W.....	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y
Naphthylamine, lBr..	vdBr	dYBr	vdBr	vdYBr	vsRBr	vdBr	vsYBr	vdBr	vsYBr	vdBr	vsYBr	vdBr	vsYBr	vdBr	vsYBr

TABLE NO. 3. COMPARATIVE INDEX FOR CHLORIC ACID.

Test solution of	(1) KClO <sub>3</sub> .	(2) H <sub>2</sub> O. KOH.	(3) KOH. KOH.	(4) dGrBr	(5) H <sub>2</sub> O.	(1) D	(2) D	(4) B	(5) D	(1) KClO <sub>3</sub> .	(2) H <sub>2</sub> O.	(3) NH <sub>4</sub> OH.	(4) NH <sub>4</sub> OH.	(5) H <sub>2</sub> O.	(1) D	(2) D	(4) C	(5) D
Phenol.....	Y	Y	dGrBr	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y
Pyrocatechol.....	sY	Y	lBr	Y	W	D	D	E	F	vsBr	vsBr	vsBr	vsBr	sBr	A	A	A	B
Resorcinol.....	sBrY	Br	YBr	YBr	sY	C	C	C	C	sBr	sBr	vsBloBr	vsBr	vdBr	B	B	A	B
Hydroquinone....	vdBr	vdRBr	dYBr	dYBr	vsBr	B	B	B	E	vsBr	vsBr	vsBr	vsBr	sBr	A	A	A	B
Pyrogallol .....																		
Cresol .....																		
Orcinol .....	MdsGr	MdGr	vdGrBr	YBr	dBr	C	C	A	B	vsBrGr	MdBr	BrY	sO	sB	A	C	C	C
Salicylic acid ....	Y	Y	YBr	YBr	YBr	D	D	C	D	Y	Y	BrY	Br	lBr	D	D	C	C
Galic acid .....	sGrBr	Br	YBr	YBr	Br	B	C	C	C	vsBrY	sBrY	sO	sO	sGrBr	A	B	C	B
α-Naphthol .....	sYBr	Br	dYBr	dYBr	Br	B	C	C	B	vsBrY	sBrY	BrY	vsBr	sGrBr	A	B	B	B
Alizarin.....	lY	Y	W	W	W	E	E	F	F	lY	lY	lY	W	W	F	E	E	E
Anilin oil .....	vdBl	vdBl	MdBr	MdBr	RPur	A	A	B	B	vdBl	vdBl	MdBr	MdBr	sGra	A	A	A	C
Dimethylanilin ..																		
Acetanilid .....	lY	O	lBr	lBr	Y	E	D	D	E	BrY	sBrY	YBr	YBr	lBr	D	C	C	D
Diphenylamin ...	vsBl					A				vsBl					A			
Orthotoluidin . . .	vdBl	vdBl	MdPur	MdPur	sBlPur	A	A	A	A	vsBl	vsBl	MdPurGra	sBl	vsBl	A	A	B	A
Paratoluidin .....																		
"Amidol" .....	lBr	sCh	dYGr	dYGr	sGrBr	E	B	B	B	lY	vsBlo	vsBr	vsBr	vdGrBr	F	A	A	A
"Metol".....	lO	lY	YBr	YBr	YBr	E	D	C	D	Y	lY	vsBloBr	vsRBr	dBr	F	E	A	B
α-Naphthylamin..	sR	sYR	vdYBr	vdYBr	dBr	B	C	A	B	sRY	sBrY	vsBr	MdvsBr	vdBr	B	B	A	B

TABLE No. 4. INDEX FOR THE ANILINS AND TOLUIDINS.

Fifteen drops of test solution of	1 drop 5 per cent. KNO <sub>3</sub> .	6 drops H <sub>2</sub> O.	KOH. H <sub>2</sub> O. (1)	(4) HClO <sub>3</sub> .	1 drop 5 per cent. H <sub>2</sub> O.	6 drops KOH. H <sub>2</sub> O. (1)	4 cc. H <sub>2</sub> O. H <sub>2</sub> O. (1)	KOH and H <sub>2</sub> O. (1)	KNO <sub>3</sub> and H <sub>2</sub> O. (1)	KOH and H <sub>2</sub> O. (1)
(1) Anilin.....	vdBr	Br	MdBr	Y A B vvsBl	vdBr	MdBr	PkBr	A A vsBr	Br Y A vsBl	dBr BrY A
(2) Orthotoluidin.	vvdBr	vsRBr	MdBr	Br A A vvsBl	sCri	MdBr	GrBl	A Bl vsPurBr	sBr Gr A vsBl	dBr Gr A
(3) Paratoluidin.	vdBr	Br	MdBr	Y A B vsBr	Br	MdBr	Br B C	vsRBr Y A vsBr	YBr Y A	Y A
(4) Anilin and orthotoluidin ....	vdBr	sBr	MdBr	Y A B vvsBl	sCri	MdBr	GrBl	A B vsPurBr	Br Gr A PurBl	dR Gr A
(5) Anilin and paratoluidin.....	vsCri	lBr	MdY	Y C B Pur	sBr	MdBr	lBr B C	vsCri Y A Pur	R BrY A	Br
(6) Anilin and both toluidins.....	Blo	sBr	MdBr	Y A B vvsBl	vsCri	MdBr	GrBl	A B vsCri	RY YGr A Cri	dBr YGr A
(7) Dimethylanilin.....	sYO	O	MdY	Y C B Y	YGr	MdBr	lBr C C	sYCri O Y B sYCri	O Y B	Y B
(8) Dimethylanilin and orthotoluidin	vsBr	Br	MdY	Y B B BlGr	RBr	MdBr	Br B B	vsRB R Gr A vsBr	R Br A	Br A
(9) Dimethylanilin and paratoluidin.....	vsBlo	lBr	MdY	Y C B vsBr	sRBr	MdBr	lBr B C	vsBlo Y YBr	*A vsBlo YBr	BrY A
(10) Dimethylanilin and both toluidins .	vsBlo	lBr	MdY	Y A B BlPur	sRBr	MdBr	lBr A C	vsBlo R YBr	*A vsBlo R	BrY A

FORMULAS USED IN PREPARING THE TABLE.

- |                         |          |                          |          |                          |          |
|-------------------------|----------|--------------------------|----------|--------------------------|----------|
| (1) Anilin.....         | 4 drops  | (6) Anilin.....          | 2 drops  | (9) Dimethylanilin.....  | 2 drops  |
| (2) Orthotoluidin ..... | 4 "      | Orthotoluidin .....      | 2 "      | Paratoluidin.....        | 0.2 gram |
| (3) Paratoluidin .....  | 0.4 gram | Paratoluidin .....       | 0.2 gram | (10) Dimethylanilin..... | 2 drops  |
| (4) Anilin.....         | 2 drops  | (7) Dimethylanilin ..... | 4 drops  | Paratoluidin .....       | 0.2 gram |
| Orthotoluidin .....     | 2 "      | (8) Dimethylanilin ..... | 3 "      | Orthotoluidin .....      | 2 drops  |
| (5) Anilin.....         | 2 "      | Orthotoluidin .....      | 2 "      |                          |          |
| Paratoluidin.....       | 0.2 gram |                          |          |                          |          |

In all cases ten cc. of concentrated sulphuric acid were used.



TABLE NO. 5. SENSITIVENESS OF VARIOUS TESTS.

Dimethylanilin, (9) Table 4.			Phenolsulphonic Acid.			Salicylic Acid.		
Ten drops of test solution and one drop of KNO <sub>3</sub> of	In a few seconds.	In ten minutes.	Ten drops of test solution and one drop 5 per cent. KCl and KNO <sub>3</sub> as before.	In ten minutes	15 drops of test solution and 1 drop KNO <sub>3</sub> as before, two minutes.	Three hours.	Two minutes.	Three hours.
5 per cent.	sCri	vsCri	sCri	vvsBlo	1Y	Y	1Y	Y
1 "	Pk	sPk	Cri	vsBlo	vv1Y	1Y	1Y	1Y
0.1 "	vlPk	lPk	Pk	sBlo	W	W	W	W
0.01 "	vv1Y	vv1Y	vlPk	lPk				
0.001 "	vv1Y	vv1Y	vv1Pk	lPk				
Hydroquinone.								
15 drops of a one per cent solution and 1 drop KNO <sub>3</sub> of	After five minutes.	After one-half hour + KOH.	Fresh solution } 0.1 gram Diphenylamin.	15 mm. No. 6, Table 4. + 1 mm. of	Anilin test for chlorates.			
			15 mm. + 7 mm. 2 seconds.	1 per cent.	2 min. 15 min.			
0.1 per cent.	Br	BrY	KNO <sub>3</sub> .	vvsBl	KClO <sub>3</sub>	vvdl	dBrR	
0.01 per cent.	lBr	vlY	0.1 per cent. KNO <sub>3</sub> .	6 seconds. sBl	0.1 per cent. KClO <sub>3</sub>	Bl	lBr	
0.001 per cent.	vlBr	W	0.01 per cent. KNO <sub>3</sub> .	0.5 minute. lGrBl	0.01 per cent. KClO <sub>3</sub>	W	vvvlBr	
			0.001 per cent. KNO <sub>3</sub> .	1 minute. No change.				

## NOTE.

*The Lavoisier Memorial.*—It is doubtless well known to a majority of the members of the American Chemical Society that it is proposed to erect a monument in Paris to the memory of the illustrious Lavoisier, and dedicate it at the time of the next French Exposition, in 1900.

The honor of suggesting this monument, or at any rate, the erection of it by popular subscription among chemists, appears to belong to the United States, as Dr. Gustavus Hinrichs, of St. Louis, first called public attention to the propriety of doing homage to the memory of the savant in this manner.

The work is being conducted under the auspices of the French Academy of Sciences, and committees have been formed in this country, England, and Germany, as well as in France, to raise funds to defray the expense of erecting a suitable monument. It is hoped that the amount secured will be sufficient to provide a monument worthy the name of Lavoisier.

Unfortunately, the committee for the United States was slow in beginning its work, but there is yet ample time to do all that is necessary if a proper response be made to the solicitations of the men who have agreed to do the work among American chemists and other friends of science. Dr. Hinrichs was made the delegate of the French Academy for the United States. He has asked the following named chemists to serve as an American committee, to whom contributions should be made :

Jasper L. Beeson, A.M., Ph.D., late Professor of Chemistry in the Audubon Sugar School ; Research Chemist for the Louisiana Experiment Station, Etc. New Orleans, Louisiana.

Charles Anthony Goessmann, Ph.D., LL.D., Professor of Chemistry at the Massachusetts Agricultural College ; Chemist at the Hatch Experiment Station of the College ; Chemist of the Massachusetts State Board of Agriculture, Etc. Amherst, Massachusetts.

Eugene W. Hilgard, Ph.D., LL.D., Professor of Agricultural Chemistry in the University of California ; Director of the California Experiment Station. Berkeley, California.

Richard Watson Jones, M.A., LL.D., Professor of Chemistry in the University of Mississippi. University, Mississippi.

John Uri Lloyd, Professor of Chemistry in the Eclectic Medical Institute of Cincinnati ; President (1887) of the American Pharmaceutical Association. Cincinnati, Ohio.

John H. Long, M.S., Sc.D., Professor of Chemistry and Director of the

Chemical Laboratories of the Schools of Medicine and Pharmacy of the Northwestern University. 2421 Dearborn Street, Chicago, Illinois.

John Ulric Nef, Ph.D., Professor of Chemistry and Director of the Kent Chemical Laboratory of the University of Chicago. Chicago, Illinois.

James Marion Pickel, A.M., Ph.D., Professor of Chemistry in the University of Alabama. University, Alabama.

Paul Schweitzer, Ph. D., Professor of Agricultural Chemistry and Chemist to the Agricultural Experiment Station, University of the State of Missouri. Columbia, Missouri.

William Simon, Ph.D., M.D., Professor of Chemistry in the College of Physicians and Surgeons of Baltimore, in the Maryland College of Pharmacy and in the Baltimore College of Dental Surgery. 1348 Block Street, Baltimore, Maryland.

Edgar F. Smith, Ph.D., Professor of Chemistry in the University of Pennsylvania; Director of the John Harrison Laboratory of Chemistry; President (for 1895) of the American Chemical Society. Philadelphia, Pennsylvania.

Eugene Allen Smith, Ph.D., State Geologist of Alabama; Formerly Professor of Chemistry, now of Mineralogy and Geology in the State University of Alabama. University, Alabama.

Henry Trimble, A.M., Ph.M., Professor of Analytical Chemistry in the Philadelphia College of Pharmacy; Editor of the American Journal of Pharmacy. 145 North Tenth Street, Philadelphia, Pennsylvania.

Francis Preston Venable, Ph.D., Professor of Chemistry in the University of North Carolina; Secretary (for 1896) of the Chemical Section of the American Association for the Advancement of Science. Chapel Hill, North Carolina.

Gustavus Detlef Hinrichs, M.D., LL.D., Professor of Chemistry, St. Louis College of Pharmacy; Delegate of the Academy of Sciences, of Paris, for the United States. 3132 Lafayette Avenue, St. Louis, Missouri.

The members of the committee have been provided with blanks and explanatory circulars, and have already sent out many to persons likely to contribute. It is hoped that all members of the American Chemical Society will feel interested in the project and will assist liberally. It should be stated that every dollar contributed will be sent to the treasurer of the fund, M. Gauthier-Villars, at Paris, as all expenses attending the collection here will be defrayed by the members of the committee.

J. H. LONG.

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### NEW BOOKS.

CHEMISTRY FOR ENGINEERS AND MANUFACTURERS. BY BERTRAM BLOUNT and A. G. BLOXAM. VOL. II. CHEMISTRY OF MANUFACTURING PROCESSES. 8 vo. 484 pp. 1896. London: Charles Griffin & Co., L't'd. Philadelphia: J. B. Lippincott Co. Price, \$2.50.

The first volume of this work, issued early in 1896, has been

reviewed in this Journal, 18, 745. The second volume is double the size of the first and contains, besides an index, a bibliography. In the latter we notice several books by American authors, but, unfortunately, many are wanting. Thus Sadtler's admirable work on "Industrial Organic Chemistry," which gives many processes connected with the topics treated of in the work before us is not mentioned. Yet the authors have endeavored to make the book attractive to American readers, and frequent references are made throughout to our methods and processes. The work is illustrated by over forty cuts and the general make up in type and paper is excellent.

There are eighteen chapters, and both inorganic and organic products, and their manufacture, are treated of.

Under the alkalies we notice an outline of the electrolytic preparation of caustic and other products, while the Solvay and LeBlanc processes receive their due share of attention.

Under the head of destructive distillation, water gas, and the enriched water gas used as an illuminant are very briefly considered. These processes do not find favor in England, though they have been greatly perfected there. Acetylene receives notice, but its position toward illuminating gas when manufactured from calcium carbide is still under trial. The enrichment of coal gas is on the increase, however, since we have a record of thirty candle power, as furnished to Edinburgh, and nearly as high to other towns. The enrichment of gas will undoubtedly be more generally practised the more gas is used as fuel, since the heating value is increased per cubic foot used, by the increase of combustible, due to added hydrocarbons.

The utilization of "basic slag" as a fertilizer is given space and a figure of the ball grinding mill used to reduce the slag to a fine powder is inserted. The Siemens tank furnace for glass manufacture is described and a figure showing cross section given. Very brief mention is made of the newer glasses for optical, thermal, and other scientific and industrial uses, whose manufacture in Germany has marked a decided advance.

Under the processes of sugar manufacture we find that of dextrose given, but no mention of Behr's method, whereby pure

anhydrous dextrose is commercially obtained by crystallization from aqueous solution.

The chapter on "Brewing and Distilling" is very short, being but an outline of the processes. This is also true of the two succeeding chapters on oils, resins, varnishes, and fats. The textiles and their bleaching are considered in a short chapter, while the theory of dyeing and dyestuffs are given considerable space. Paper, pigments, and paints form a couple of chapters. Leather and glue receive quite a proportionate amount of attention.

It is of course extremely difficult to condense so many and such varied topics into a book of this size, but the authors have discriminated on the whole wisely.

Above all things, it is to be noted with some satisfaction that chemical engineering problems are coming more to the front and that books of this character are multiplying. That the authors are live men the writer had an opportunity to judge from an inspection of a highly interesting exhibit by Mr. Blount, at the Institute of Civil Engineers. The apparatus was devised especially to meet the demands coming from engineers regarding important problems as the estimation of oxygen in copper, the quality of boiler scale produced by waters, etc.

He also had the pleasure of listening to an able lecture by Mr. Bloxam before an audience of gas engineers. The topic was the recovery of cyanogen compounds from gas works. The various lines of procedure for recovering these now most useful products were detailed as were also the uses to which the products could be put.

It is to be hoped that manufacturers, especially in the United States, will, through just such treatises, be led to see the value of chemical knowledge and skill for the proper control of their works and thus stimulate young men to undertake studies which will more fully fit them for responsible positions.

C. A. DOREMUS.

THE DEVELOPMENT OF THE PERIODIC LAW. BY F. P. VENABLE, PH.D., F.C.S. Easton, Pa.: Chemical Publishing Co. 1896. viii + 321 pp Square 12mo. Price, \$2.50.

The author of this important work, who is Professor of Chemistry in the University of North Carolina, has already become

favorably known by his "Short History of Chemistry," (Boston, 1894.) When one undertakes to write the history of events that have taken place in several countries of Europe, it is a great advantage to be an American, as this insures more candor and impartiality than is likely to characterize a European author. Professor Venable shows extensive acquaintance with the literature of his subject and good judgment in the selection of materials.

In a prefatory sketch the author gives a condensed summary of the development of the periodic law, the details of which are elaborated in eight succeeding chapters; in this he expresses the feeling that the system is far from complete: "The close of this century calls loudly for another Lavoisier who shall interpret the facts won by such hard toil and place the science on the right track for another century of brilliant progress and discovery."

In the first chapter he discusses the hypothesis of Prout and the triads of Doebereiner, with the views of Berzelius, Dumas and others, respecting the numerical relations of the atoms. The latter topic is treated more at length in Chapter II. Then follows some account of Brodie's Ideal Chemistry, of the telluric screw of de Chancourtois, and of the law of octaves proposed by Newlands; the contributions of many minor lights to the general subject are not overlooked, as, for example, the propositions made by Kotikovsky, by Lenners, by Hinrichs (pantogen), and others.

Of course Lothar Meyer and Mendeléeff receive the most attention, and their share in founding the periodic law is most conscientiously given.

The writer of this can supply a single item from personal knowledge: the author of the anonymous paper on the Pairing of the Elements, which appeared in the American Supplement to the New York edition of the *Chemical News*, in 1869, was the late Professor Charles A. Seeley, of New York.

As one reads this valuable contribution to the history of an idea, one is struck with the number of persons who have contributed in a lesser measure to the general subject; thus, we find the names of Gibbs, Zängerle, Crookes, F. W. Clarke, Bayley, Carnelley, Rydberg, Bazaroff, Tchitcherine, Sutherland, Bassett, Flavitzky, and a host of others.

The work is not illustrated in the sense of containing pretty pictures of complicated apparatus copied from foreign books rather out of date, but it does contain representations of many diagrams, such as the spiral of von Huth, the diagrams of W. Spring, of W. Crookes, of Flavitzky, and the "generation tree" of Wendt.

A valuable feature of this work is the "Index to the Literature Relating to the Periodic Law," containing 267 titles. The book is well indexed.

This contribution to the history of chemistry will prove of use to all those interested in studying great questions which influence the progress of science.

H. CARRINGTON BOLTON.

ROENTGEN RAYS AND PHENOMENA OF THE ANODE AND CATHODE. BY EDWARD P. THOMPSON, M.E., E.E. Concluding chapter by PROF. WM. A. ANTHONY. New York: D. Van Nostrand Co. xvi, + 190 pp. Price, \$1.50.

This book is a mere compilation of 210 abstracts from various scientific journals and original memoirs. Mr. Thompson makes no attempt at classification or analysis, but has done the work hastily and superficially, by his own confession, apparently to meet the popular demand for illustrated books on this subject. There are many blunders, both in fact and in style, and the book will hardly commend itself to anybody who has access to one or two of the various scientific journals. Prof. Anthony's chapter is by far the best part of the book, as it gives a succinct and intelligible resumé of the various theories that have been advanced by Roentgen's discovery. It is to be regretted, however, that Hertz's researches on radiant electricity have received such scant attention; since they are not only the direct cause of the work of Lenard and of Roentgen, but also contain much that must be taken into account in all later speculations. It would also seem to the reviewer that Prof. Anthony does not do sufficient justice to those hypotheses which involve "free energy," not directly fastened to particles of substantial matter.

MORRIS LOEB.

THE CHEMISTRY OF DAIRYING. By HARRY SNYDER. viii + 156 pp. Easton, Pa.: Chemical Publishing Co. Price, \$1.50.

This is the title of a manual of 156 pages devoted to the chemistry of the dairy, especially in respect of the manufacture of

butter and cheese, and the methods of feeding dairy cows. This book is a significant indication of the change which has taken place in the last few years among intelligent farmers and dairymen in regard to the methods of conducting their business. As a result of the education which has been given by the agricultural colleges and experiment stations, the dairy industry of this country is rapidly assuming a scientific character. The fact that a book such as the one which has been mentioned above can be printed and sold would be sufficient evidence of this, were it not seen also in the improvement in quality and the increase in quantity of dairy products. The book has been prepared with the object of furnishing useful information to a class of young men who intend to become farmers and dairymen rather than to scientific experts. The difficulty of preparing such a book is admittedly great, especially when written by a scientific man. It is hard to draw the line between a truly scientific exposition of a subject and the maudlin mouthings of kindergartenism. The author is to be congratulated upon having steered his course very satisfactorily between the Scylla of science and the Charybdis of baby talk. The intelligent dairyman is furnished with useful information in regard to the character of the products with which he is working, the methods of determining, in an approximate manner, their chief characteristics and the proper methods to be pursued in selecting dairy animals and feeding them for the highest product.

Chapter 2, on milk testing, Chapter 10, on sanitary conditions, and Chapter 14, on the effects of food upon dairy products, are of especial interest to dairymen.

A good book would not be quite perfect without some minor defects, and Mr. Snyder's work has not entirely escaped. One cannot see, for instance, why he describes the fat particles as "rubber balls," on page 2, and milk sugar as resembling "confectionery sugar without any sweet taste." In describing the amount of butter-fat in the solids of cream he states, on page 46, that it is from eighty to ninety per cent., while in the table giving the average composition of cream a simple computation will show that it is only seventy-seven per cent. On page 5 it is said that butter should contain about eighty-three per cent. of butter-fat, while on page 54 that num-



ber is given as its minimum content. The spelling of lactocrite and Feser, on pages 112 and 113, might be improved, as likewise the grammar in such a phrase as "there is rarely less than 12 pounds," on page 3. These are minor defects which the author will not fail to correct in a second edition, which, from the excellence of the work, will doubtless soon be demanded.

**THE CONSTANTS OF NATURE. PART V. A RECALCULATION OF THE ATOMIC WEIGHTS.** BY FRANK WIGGELSWORTH CLARKE. New Edition. Revised and enlarged. City of Washington. Published by the Smithsonian Institution. 1897. 8vo. vi + 370 pp.

The first edition of this work was published in 1882. Since then, and partly, no doubt, incited by that publication, a great deal of very excellent work upon atomic weights has been done. The appearance of Professor Morley's classical work on the relative atomic weights of oxygen and hydrogen has, especially, rendered possible a new calculation based on the hydrogen unit which will command universal acceptance among chemists. The present work is carried out on the same lines and with the same painstaking accuracy as the first edition. The exact means by which the final result is obtained is given in each case. While in the selection of the final value for each element due weight is given to chemical as well as mathematical evidence, there is also given for each the result of the purely mathematical combinations obtained by weighting each observer's value in accordance with the probable error. The comparative worthlessness of the probable error as showing the value of an atomic weight determination, and the necessity of considering chemical evidence as well, in spite of the objectionable "personal equation" introduced, is well shown by the fact that the probable error for oxygen as given by Professor Clarke in 1882 was 0.0035, while the present value differs from that then given by more than twenty-four times that amount.

The present work is, undoubtedly, the best available summary of our knowledge of atomic weights. W. A. NOYES.

**TABLES FOR IRON ANALYSIS.** BY JOHN A. ALLEN. vii + 85 pp. New York: John Wiley and Sons. Price \$3.00.

The author states in his preface that serious discrepancy only exists in the atomic weights of magnesium and silicon, and, in

iron laboratories, these are used only for the determination of constituents which occur in small quantities. The amount of silica in slags and magnesia in slags and dolomitic limestones does not accord with this statement. A difference in the atomic weight of magnesium would also affect the determination of phosphorus as magnesium pyrophosphate. The commas should be omitted from some of the tables, and if they were arranged for one gram of sample and to cover larger percentages, they would be more valuable and much simpler.

More examples should be given to illustrate the manner of using the tables. Table XL should be headed "Factor Weights," and Table XLI "Atomic Weights." The tables are undoubtedly of value, but the arrangement might be much simplified.

EDWARD K. LANDIS.

**INORGANIC CHEMICAL PREPARATIONS.** BY FRANK HALL THORP, PH.D.  
238 pp. Boston: Ginn and Co. Price \$1.60.

In this book are found directions for the preparation of nearly one hundred compounds. Naturally enough, the salts of sodium, potassium, aluminum, ammonium, and iron receive the greater attention, but the remaining preparations are numerous and well selected, although no element is found among them.

The introductory remarks concerning solution, precipitation, filtration, evaporation, etc., are clear, full, and satisfactory, and the directions are, in most instances, all that could be desired. In some cases, however, the methods given would not furnish chemically pure substances.

Nearly all questions, that a student might ask, are anticipated and answered, while the use of equations to explain the chemistry of the methods and the incorporation in the text of numerous tables of solubility and specific gravity add not a little to the usefulness of the book.

In an appendix are placed specific gravity tables of the more common acids and ammonia, and a table showing atomic weights and valence.

The paucity of books of its kind and quality in the English language makes its appearance most welcome. L. B. HALL.

**NITRO-EXPLOSIVES.** BY P. GERALD SANFORD. 8vo. 270 pp. 54 Illus.  
London: Crosby, Lockwood and Son. 1896. Price, 9 shillings.

The sub-title states that this book is a "Practical treatise con-

cerning the properties, manufacture, and analysis of nitrated substances, including the fulminates, smokeless powders and celluloid." A treatise to be practical should be first of all reliable, and second, it should be written in so clear and direct a manner that its descriptions may be easily and definitely understood by intelligent readers. The book before us is an example of the reverse of this, in that it is filled with errors and is so involved in its style that it is doubtful if any one but an expert could tell what it was that the author really sought to say.

As an example of the errors in the book we call attention to the description of the Boutmy & Faucher process of making nitroglycerine. This process is one of those best known to book-makers; it has especially interested chemists, as its invention is believed to have arisen from the consideration of Berthelot's second thermo-chemical law; the invention was crowned by the French Academy; and the process has been repeatedly described, the reviewer having himself, as long ago as 1878, published an account of his visit to the works of the French Government at Vonges, where this process was operated, yet on page 16 of his book Mr. Sanford says, "A few years later (1872) M. M. Vouges and Boutmy\* proposed to prepare nitro-glycerine by mixing the sulphuric acid with glycerine," etc., etc. The asterisk refers to the foot-note, " \* *Comptes Rendus*, 75, and Desortiaux, *Traité sur la Poudre*, 684-686," and turning to the latter we read: "Le procédé employé depuis 1872 à la poudrerie des Vonges, et dû aux recherches de H. Boutmy et de L. Faucher," etc., etc. Throughout the book we find everywhere evidence of haste and negligence, so that one wonders why, if the author was unable to give the proper amount of time and effort to the preparation of the book, he should have undertaken it at all, and especially as no "long-felt want" existed for such a book.

The author states in his preface his belief "that the account given of the manufacture of nitroglycerine and of the gelatine dynamites will be found more complete than in any similar work yet published in this country," but a comparison with "The Manufacture of Explosives" by Oscar Guttman, published in London the previous year, shows that this earlier book devotes more than double the space to the treatment of these topics, and deals with them in a more systematic and thoughtful manner.

The chief merit of Sanford's book lies in the fact that he has collected and presented more information regarding analytical methods than is, to my knowledge, to be found in any one place, and if he had given his entire thought and attention to the elaboration of this material he would have produced a book of value and one which must have contributed to his professional reputation. As it is he has given us a crude work.

I am especially sorry to give this adverse opinion of his book, since Mr. Sanford quotes more freely from and oftener gives credit to American investigators than any other European writer on this subject.

CHARLES E. MUNROE.

**A SIMPLE METHOD OF WATER ANALYSIS, ESPECIALLY DESIGNED FOR THE USE OF MEDICAL OFFICERS OF HEALTH. BY JOHN C. THRESH, M.D., D.Sc. 49 pages. 1897. Philadelphia: P. Blakiston, Son & Co., and London: John A. Churchill. Price 88 cents.**

The book before us is one intended to so simplify the method of water analysis as to bring them within the power of the "Medical officers of health for rural districts" to accomplish, any such officer being "well aware that unless he himself can undertake the work it must remain undone."

The analytical processes described "require no specially fitted laboratory, and only the simplest possible apparatus," and the analysis "can be conducted in the neighborhood of the well or other source of supply."

The chemicals used are in the form of "Soloids" each containing exactly the requisite quantity, and they remind one of the "Fehling's Test" capsules now supplied to the medical profession.

That the book can fulfil any useful mission in this country is exceedingly doubtful. The processes described can give but approximate results at the best, and are such as would not be acceptable to a health officer were he a chemist, for the sufficient reason that he would be in a position to employ more exact methods. Should the officer in question not be a chemist he would be wise to omit analytical examination entirely, and content himself with a careful sanitary survey of the surroundings of the source of supply.

W. P. MASON.

**THE COTTON PLANT.—ITS HISTORY, BÓTANY, CHEMISTRY, CULTURE, ENEMIES, AND USES.** Washington: Government Printing Office, 1896. 433 pp.

This is the title of Bulletin No. 33, issued by the Office of Experiment Stations of the Department of Agriculture. To all persons who are seeking for convenient and compendious information on this important plant, this bulletin will be of the greatest value. The parts which chiefly concern the readers of the Journal are the articles on the Chemistry of Cotton, prepared by J. B. McBryde and W. H. Beal, and the feeding experiments, by B. W. Kilgore. With commendable industry and research the compilers have brought together in convenient form for reference the analytical data scattered through journals and other sources, as a rule quite inaccessible to chemists at a distance from large libraries. The collated analyses treat of the entire plant, the roots, stems, leaves, bolls, lint, seed, hulls, oil, and seed cakes. The mean composition of the entire plant, of all its various parts, and of the products of its seed are given from all available data. The article on the feeding value of the seeds contains a résumé of the feeding experiments which have been conducted in this and other countries, arranged in such a manner as to secure in an easily accessible form the data of greatest importance. In this connection the reviewer would beg leave to suggest that the data relating to the injurious effects of feeding cotton-seed cakes to young animals would have had a greater value by being collected into a separate paragraph. Of particular interest to dairy chemists is the section relating to the effect of cotton-seed diet on the composition of butter.

In the article on the Chemistry of Cotton there is a paragraph relating to the carbohydrates of the cotton-seed which is hardly in harmony with the excellent character of the rest of the material and with our present knowledge of that subject. As is well known, the predominant sugar of the cotton-seed is raffinose and the described sugar, melitose, is now believed not to exist, or at least to be only an unstable union of raffinose with eukalyn. Repeated attempts of later and expert workers to isolate the so-called melitose from cotton-seeds have entirely failed. Tollens admits the term melitose as one of the synonyms of raffinose, but von Lippmann does not. On page 95

it is stated that Ritthausen describes "methods for separating melitose in crystalline forms, etc., and also gives some of its chemical and physical properties." Tollens, who reviewed the work of Ritthausen, established beyond question that these crystals were pure raffinose, and that the mythical substance, melitose, does not occur in cotton-seed, if it does exist in manna exuded from the *Eucalyptus viminalis and gunnii*. (*Ztschr. der Vereins für Rubenzuckerindustrie*, 85, 591, and 86, 217.)

Berthelot examined the Eucalyptus mannas above mentioned and gave the name melitose to the sugar they contained.<sup>1</sup> Subsequently he re-studied the material and came to the conclusion that his former statements were incorrect and he was convinced that melitose as such did not exist, but he kept the name for a preparation of raffinose from cotton-seed, which he secured in the cold, and which he supposed to be a very unstable compound with eukalyn.<sup>2</sup> No other investigator has ever been able to isolate this body and it is doubtless a myth. Even the existence of eukalyn is not certainly established. In the light of our present knowledge it seems that the term *gossypose* found on page 96 of the bulletin as an alternative name for melitose is the preferable characterization for this hearsay sugar.

### BOOKS RECEIVED.

Bulletin No. 39. The Peach. Texas Agricultural Experiment Station, College Station, Brazos County, Texas. July, 1896. 48 pp.

El Kambio de Komposition ke Esperimenta el Agua de "el Salto." By K. Newman, Santiago de Chile: Imprenta i Enkuadernazion. Poma. 1896. 14 pp.

Inorganic Chemical Preparations. By Frank Hall Thorp, Ph.D. iv + 238 pp. Boston: Ginn & Co. Price, \$1.60.

Bulletin No. 42. I. Analyses of Manurial Substances sent on for Examination. II. Analyses of Licensed Fertilizers collected by the Agent of the Station during 1896. III. New Laws for the Regulation of the Trade in Commercial Fertilizers in Massachusetts. October, 1896. Hatch Experiment Station of Massachusetts Agricultural College, Amherst, Mass. 32 pp.

Physical Laboratory Manual for Secondary Schools. By Charles F. Adams, A.M. Chicago and New York: Werner School Book Co. 183 pp. 1896.

<sup>1</sup> *Ann. chim. Phys.* [3], 46, 66.

<sup>2</sup> *Compt. rend.*, 103, 533.

# THE JOURNAL

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[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF PURDUE  
UNIVERSITY.]

## THE QUANTITATIVE DETERMINATION OF CARBOHY- DRATES IN FOOD STUFFS.

BY W. E. STONE.

Received February 2, 1897.

IN various articles published by the author<sup>1</sup> during the past ten years, attention has been called to the character of the composition of the so-called "nitrogen-free extract" of food materials. Other writers<sup>2</sup> have also discussed the same subject and numerous specific researches have contributed a constantly increasing amount of definite knowledge bearing upon the matter. As a result, it is now generally recognized that that portion of food material broadly included under the term "nitrogen-free extract," consists of a considerable number of definite chemical compounds, mostly of the nature of carbohydrates, but of such evident variation as regards their food value or digestibility, as well as their chemical and physical properties, that it is highly inconsistent, if not absurd, to continue to regard them as of homogenous character or worth in food valuation.

When one refers to the very great number of food analyses now on record and notes how large a proportion of all vegetable foods consists of nitrogen-free extract, he cannot escape the thought that a more definite knowledge of this group of bodies

<sup>1</sup> *Am. Chem. J.*, 13, 73; 14, 9; 15, 653; 15, 660; *J. Anal. Appl. Chem.*, 5, 421; *Agri. Sci.*, 2, 315; 7, 6; U. S. Dept. Ag. Div. Chem., Bull., 28, 125; *Ber. d. chem. Ges.*, 23, 3791; 24, 3019; 25, 563; *Proc. Am. Asso. Advancement of Science*, 31, 159; *Proc. Soc. Promotion of Agr. Science*, 1890.

<sup>2</sup> See articles by Tollens and his colleagues in *J. f. Landwirtschaft, Versuch-Stationen*, etc.; H. Schulze, *Ber. d. chem. Ges.*; and Cross and Bevan, *J. Chem. Soc.*

is necessary, if any value is to be attached to work of this kind. Occasionally a statement of analysis may be found which refers to carbohydrates instead of nitrogen-free extract, but the same thing is meant in either case, and the results have been obtained by the same methods. In comparatively few cases is there any record of any analyst having attempted to estimate directly in a food analysis any of the various substances included under nitrogen-free extract; and anything like a complete determination of all these has rarely if ever been attempted. The present method, as almost universally followed for estimating the constituents of foods, consists in directly determining the amounts of moisture, ash, fat, fiber, and proteids in the material and the difference between the combined percentages of these and 100 is called nitrogen-free extract. This amounts, in many of the most important food materials, to more than fifty per cent. of the whole. It includes, of course, all of the known carbohydrates and doubtless other materials of unknown character, but gives no clue to the relative proportion of any of them.

In brief, the present stage of food analysis leaves us largely ignorant as to the character and value of the principal constituents of many of the most important foods. Little wonder that many have come to regard the ordinary food analysis as contributing little information regarding the actual food value of any material. It certainly affords no means of ascertaining whether the sixty to eighty per cent. of nitrogen-free extract in grains is to be valued as an easily digested carbohydrate or a practically valueless gum or hemicellulose; it tells us nothing as to the presence or absence of sugar or soluble forms of starch or their relative proportions; it furnishes, in short, no accurate information as to the quantity or quality of the carbohydrates which constitute one of the three essential classes of nutrients and are among the chief constituents of vegetable foods.

Recent contributions to our knowledge of the carbohydrates have revealed to a surprising degree not only their specific chemical and physical properties, but indicate even more subtle and delicate distinctions as regards their physiological values; their susceptibility to organized and unorganized ferments; their origin and functions in the growing plant, etc. The time is therefore fully ripe when analytical methods ought to show equal progress



and differentiate sharply between the various kinds of carbohydrates. That something of the kind is highly important will be acknowledged, I think, by every chemist who has to deal with this subject. That such a practice is not already established is due, without doubt, to the lack of general information with regard to the properties of these different substances and the absence of an accurate and easily performed method of separately estimating their amounts.

Any method of analysis intended to apply to this case and which shall be expected to become generally adopted, must have the qualities of simplicity and accuracy. It must be borne in mind, however, that the class of materials included under the general head of nitrogen-free extract, are of such a nature as to render them in many cases difficult of accurate determination.

It is believed that the method here presented satisfies these requirements better than any yet proposed. Although as here presented, some details have been modified, the general method has been employed in an investigation upon the carbohydrates of wheat and maize, the results of which have been published by the U. S. Department of Agriculture as Bulletin 34 of the Office of Experiment Stations. The analytical data presented here are selected in part from this report by permission.

The carbohydrates to be found in food materials of a vegetable origin, include sugars of different kinds, starch in various modifications and a certain kind of material, intimately associated with the true cellulose, variously designated as gums, pentosans, hemicelluloses, oxycellulose, and finally the cellulose itself.

For the determination of many of these substances, methods already exist which permit of very fairly accurate determinations, but these methods, as a rule, assume that all other carbohydrates shall be absent so that their application to a material containing several of these substances would lead to serious errors and false conclusions. The most notable example of this is the determination of starch, the ordinary method for which consists in heating the starch containing materials with dilute acids and determining the sugar thus produced by titration with Fehling's solution.

This, as well as other methods for the determination of starch in the absence of other carbohydrates, is of practically sufficient

accuracy, but as has been shown, none of these methods are applicable to the determination of starch in the presence of such other carbohydrates as the pentosans or the hemicelluloses.<sup>1</sup>

Again, the methods proposed for the determination of the pentosans are all based upon a destructive distillation of the original material with strong acids and the subsequent determination of the furfural thus produced. However accurate this final determination may be according to one or the other of several methods, it is obvious that only an approximate knowledge is obtained as to the actual amount of pentosans present in the original material.

It seems also desirable that any plan for the differentiation of carbohydrates in any given material, should, so far as possible, approximate the selective action of the digestive organs in dealing with these same materials. This principle has been recognized in the familiar Weender method for the estimation of crude fiber, which has so long been made use of by food chemists. For example, those substances which are readily soluble in mild reagents will evidently be more easily digested and assimilated than those which are practically insoluble, so that although we may not possess complete knowledge of these same insoluble substances or of their value as food materials, we may still separate them in our analytical tables from those of which we do know more and which evidently have a greater food value.

The following method for the detailed determination of the carbohydrates in vegetable materials is based upon the successive treatment of the same sample: 1, with boiling alcohol to remove sugars; 2, with cold water to remove dextrin and soluble forms of starch; 3, with diastase or malt infusion to remove starch; 4, with dilute boiling hydrochloric acid to convert the gums, pentosans, hemicelluloses, etc., into soluble, reducing sugars; 5, with boiling 1.25 per cent. sodium hydroxide, as is customary in the determination of the crude fiber by the Weender method, leaving behind crude fiber.

In all of these successive operations, linen filters are to be used in order to facilitate the subsequent removal of the sample. With very fine starchy materials it may be advisable to fold a paper filter within the linen one.

<sup>1</sup> This Journal, 16, 726.

In each of the above successive extracts the respective carbohydrates may be estimated by optical or chemical methods, although they are all susceptible of titration by Fehling's solution in the ordinary way.

This method presents certain marked advantages :

1. It permits of the estimation of these constituents in one and the same sample.
2. The process consumes comparatively little time.
3. The final determinations are made by methods already in common use, well understood, and capable of being accurately performed by persons of no great analytical skill.
4. If, by any error of manipulation, any portion of the carbohydrates sought for at any stage escapes solution, it can scarcely fail to be obtained at the succeeding stage, and so there can be no failure to sum up in the end all of the carbohydrates actually present. For instance, any sugar escaping solution in alcohol would be removed by the subsequent treatment with water. Any starch not dissolved by the malt extract would certainly be removed in the subsequent treatment with dilute acid.
5. No violence is done to our present classification of food constituents, only those portions not heretofore classified being separately estimated and recorded. Even the crude fiber remaining after this treatment would be fairly comparable with that determined by the Weender method.

The successive operations may be outlined as follows :

1. The material being finely powdered or grated, from 50 to 100 grams, according to its nature, are accurately weighed and boiled with 500 cc. of strong alcohol, under a reflux condenser, during two hours, or the material may be extracted with boiling alcohol in a Soxhlet extractor. The sugars are thus dissolved and removed by filtering off the alcoholic extract. If this contain only sucrose it may be brought to a given volume and estimated in the polarimeter. If more than one kind of sugar, as for instance sucrose and invert sugar, are present, the alcohol may be carefully evaporated, the sugars taken up in water to a given volume and estimated by titration with Fehling's solution before and after inversion, according to the ordinary treatment in such cases.

2. *The residue from the alcoholic extraction may contain carbo-*

hydrates soluble in water, as for instance soluble starch and dextrin, which are specially to be considered in materials which have been subjected to the action of heat. To this residue, therefore, is added 500 cc. of water and the whole allowed to stand eighteen to twenty-four hours with frequent agitations. The watery solution is then filtered, using a linen filter. With ordinary materials where only dextrin-like substances are to be expected, this filtrate may be evaporated to a small volume, inverted with dilute acids, and titrated with Fehling's solution in the ordinary way. If, however, the solution contain soluble starch in any of its forms, which may be recognized by the iodine test, a further distinction between this starch and dextrin becomes necessary.<sup>1</sup> The watery solution is brought to a volume of 200 cc., and of this an aliquot part is inverted with dilute acid and titrated with Fehling's solution in order to determine the total carbohydrates in the solution. Another aliquot part may be treated with an excess of a solution of barium hydroxide, which precipitates the soluble starch. In the filtrate from this precipitate, the dextrin may be determined by inversion and titration as before. The difference between the dextrin and the total carbohydrates determined in the first aliquot portion may be considered as soluble starch. The use of barium hydroxide for the estimation of the soluble starch directly, according to Von Asboth's method, is not permissible in this place because there are other substances in solution besides starch, which seem to combine with the alkali.<sup>2</sup>

3. *The residue from the aqueous extract* of the material is now brought to an air-dried condition and its weight determined in order to establish its quantitative relations to the substance as originally weighed out. This step is advisable because smaller portions are more conveniently employed for the subsequent operations.

This material now contains the starch and other insoluble carbohydrates. Two grams are weighed, 100 cc. of water added

<sup>1</sup> By soluble starch is meant starch soluble in water but still giving the characteristic blue color with iodine, in distinction from some of the more completely broken down forms of starch, like dextrin, which no longer give blue or purple colors with iodine. In only rare cases would it be necessary to make this distinction.

<sup>2</sup> It is thought that barium hydroxide combines with the albuminous substance in solution. At least a much larger amount is precipitated than can be accounted for by the total amount of carbohydrates present.

and boiled thoroughly for thirty minutes in order to convert the starch into a soluble form, then cooled to 60° C. In the meantime an infusion of malt has been prepared as follows: Ten grams of finely ground fresh malt are covered with fifty cc. of water and kept at an ordinary temperature, with frequent agitation, from two to three hours, filtered, and ten cc. of the infusion added to the starch paste, cooled as above.

The starch is subjected to the action of malt extract at a temperature not exceeding 65° C. from two to three hours, or until the blue starch reaction with iodine disappears. The solution is filtered on a linen filter and washed thoroughly with hot water. In many cases this filtration will be facilitated by previously heating the solution to boiling and filtering hot. The residue on the filter should give no starch reaction with iodine. The filtrate is evaporated to 100 cc., transferred to a 200 cc. flask, receives ten cc. of concentrated hydrochloric acid, and the flasks with contents kept at the temperature of a boiling water bath for one hour in order to convert all of the malt sugar into dextrose. The solution is then neutralized, made up to a volume of 200 cc., and titrated with Fehling's solution. A correction must of course be employed for the amount of sugar introduced in the malt extract.

4. *The residue from the malt extraction* still contains the gums, pentosans, hemicelluloses, and true cellulose. It is carefully removed from the filter, receives 100 cc. of water and two cc. strong hydrochloric acid, and is heated to boiling under a reflux condenser or in a water bath for one hour.

The action of the acid converts the gum and pentosans into reducing sugars, which may be regarded as xylose.<sup>1</sup> This is then filtered, neutralized, made up to 200 cc. and titrated with Fehling's solution.

5. We have now reached a stage corresponding to that attained in the determination of crude fiber by the Weender

<sup>1</sup> Repeated examinations of the character of this material shows that in most of the fibrous or woody vegetable materials it is xylan and yields on hydrolysis mainly xylose. This is the case especially in all materials containing any considerable amount of hydrolyzable carbohydrates of this kind, although in some special cases mannose, galactose, or arabinose have been noted as products of this treatment. It is thought sufficient, however, for all general purposes to regard this product as xylose, since the error introduced by the varying reducing coefficients of small amounts of the other sugar would be nominal.

method after the material has been boiled with one and one-fourth per cent. sulphuric acid. It remains, therefore, to treat this residue with 1.25 per cent. sodium hydroxide, to filter, dry, weigh, ignite and weigh again, in order to obtain what is commonly known as "crude fiber."

It is necessary now to consider the accuracy of each of these steps in detail, and to present examples of their application. For the purpose of illustration the following materials have been examined according to the plan here presented: Wheat, two samples; wheat flour, two samples; maize; bread made from each of the samples of whole wheat, flour, and maize; sugar beets, and a sample of timothy hay.

#### I. THE ESTIMATION OF SUGARS BY EXTRACTION WITH BOILING ALCOHOL.

It is hardly necessary to discuss this method since it is the generally accepted way of separating sugars from other materials either for qualitative or quantitative analysis. All of the ordinary sugars are soluble in boiling alcohol of ninety-five per cent. strength, especially when sufficient volume is employed as is the case in the specifications of the method here presented. It is even applicable to fresh materials, such as the sugar beet, potato, etc., in the presence of a large amount of moisture.

In the treatment of many materials, the hot alcohol also dissolves waxes and oils, which are readily removed by evaporating the solution nearly to dryness and then taking up in water. The polarimeter may be employed in many cases for determining the sugar thus extracted, in preference to the method of inversion and titration.

The following examples will serve to show how sugars, in small or large quantities, may be determined in a variety of materials and with accuracy, by means of this method:

#### SUGAR OBTAINED BY EXTRACTION WITH BOILING ALCOHOL.

	Sucrose. Per cent.	Invert sugar. Per cent.
Wheat I .....	0.51	0.08
Wheat II .....	0.72	0.00
Wheat flour I .....	0.18	0.00
Wheat flour II.....	0.20	0.00
Maize .....	0.27	0.00
Sugar beet (Fresh) .....	8.38	0.07
Hay (Timothy).....	2.53	0.00

	Sucrose. Per cent.	Invert sugar. Per cent.
Bread (Whole wheat I).....	0.05	0.32
Bread (Whole wheat II) .....	0.06	0.37
Bread (Wheat flour I) .....	0.01	0.10
Bread (Wheat flour II) .....	0.15	0.38
Corn cake (Maize).....	0.16	0.19

## 2. THE ESTIMATION OF DEXTRIN AND SOLUBLE STARCH.

These materials, while insoluble in alcohol, are readily dissolved in water at ordinary temperature.

Usually grains and seeds in their natural condition contain very small quantities of materials of a carbohydrate nature, insoluble in alcohol and soluble in cold water which it is sufficient to designate here as dextrin. Some attempts to identify these bodies in a more specific manner, have been made. In this place, however, it is only necessary to say that they are readily changed into sugars by inversion with acids and behave, to all intent and purpose, like dextrin. If, however, the material has been subjected to heat or friction, as in the grinding of corn or flour, or to the action of acids, then a portion of the starch may have been changed into soluble forms and will accompany the dextrin in the watery solution. The presence of such starch will be readily detected by means of the blue color produced with iodine.

In the absence of such starch, it is sufficient to estimate the dextrin by inversion with acids. When, however, soluble starch is present, the separate estimation of the two becomes a more difficult matter. Ordinarily the small amount of dextrin would render a separate estimation of the two hardly necessary, in which case the watery extract might be at once inverted with acids and the total soluble carbohydrates estimated in this way.

Evidently there will be little occasion to assign different values to these two forms of starch products even after they are separately estimated. If desirable, however, the starch may be completely precipitated with barium hydroxide, according to the plan proposed by Von Asboth, and a separate estimation made as indicated above.

These separations have been made in some of the analyses presented below, and there is no reason to doubt that they are sufficiently accurate.



## DEXTRINS AND SOLUBLE STARCH EXTRACTED BY COLD WATER.

	Dextrin. Per cent.	Soluble starch. Per cent.
Wheat I.....	0.27	0.00
Wheat II .....	0.41	0.00
Wheat flour I.....	0.90	0.00
Wheat flour II.....	1.06	0.00
Maize .....	0.32	0.00
Sugar beet (Fresh) .....	0.35	0.00
Hay .....	1.18	0.00
Bread (Whole wheat I).....	0.68	1.37
Bread (Whole wheat II) .....	0.23	2.36
Bread (Flour I).....	0.27	1.99
Bread (Flour II).....	0.91	1.74
Corn cake (Maize).....	0.00	2.80

## 3. THE ESTIMATION OF STARCH BY TREATMENT WITH MALT EXTRACT.

The residue from the preceding treatment consisting of many grams of material, is too bulky for subsequent operations. In order, therefore, to secure smaller portions of definite quantitative relations to the original fifty or one hundred grams taken, these residues are desiccated, weighed, and the amount of dry matter contained therein is determined. The proportion between this dry matter and that in the original material may then be established. From this, then, two grams are taken for the determination of starch and other remaining carbohydrates.

Many methods have been proposed for the determination of starch, any of which are fairly satisfactory when applied to starch in the absence of the other carbohydrates. A review of these methods and comparison of their values will be found in a former paper by the author,<sup>1</sup> and also in papers by H. C. Sherman<sup>2</sup> and by P. Hibbard,<sup>3</sup> but all of these methods give inaccurate results when applied to materials which contain any of the pentosans or gums or easily hydrolyzable forms of cellulose, since these latter materials are affected in the same way as starch and give similar products with the same reagents.

They are not, however, appreciably affected by the action of diastase,<sup>4</sup> and thus far it appears that this is the only agent which

<sup>1</sup> This Journal, 16, 726.

<sup>2</sup> *School of Mines Quarterly*, Columbia College, 17, 356.

<sup>3</sup> This Journal, 17, 64.

<sup>4</sup> The somewhat obscure action of malt extract on cellulose mentioned by Brown and Morris, as well as a similar action upon hemicelluloses, is of very uncertain extent under any conditions and is practically checked at 60°. J. Grüss: *Wochenschr. Braueri*, 1895, 1257.



may be employed for the accurate separation of starch from these other substances.

As to the efficiency of this method for the complete removal of starch, there seems to have been some question. It also appears from recent investigation by the author that not all starches are affected in the same manner or degree by diastase. It may be found necessary in different cases, to subject the material to the action of diastase for a longer or shorter time. The operation, however, is wholly within the control of the analyst, since the final extraction of starch from the material can be detected by the iodine reaction. Being once in solution, it is then readily separated from the insoluble residue and converted into sugar by the action of dilute acids as above described.

The following table shows the results obtained upon the material previously extracted and examined for other carbohydrates as described above.

These data were obtained by the use of more dilute acids for the hydrolysis of the malt extract, than is recommended above. The percentages are therefore somewhat lower than those usually ascribed to these materials. With the strength of acid prescribed there is no difficulty in obtaining complete conversion of the starch products into sugar.

#### NORMAL STARCH DISSOLVED BY MALT EXTRACT.

	Per cent.
Wheat I.....	30.94
Wheat II.....	30.36
Wheat flour I.....	46.19
Wheat flour II.....	34.04
Maize .....	42.50
Sugar beet( Fresh).....	0.00
Hay.....	7.49
Bread (Whole wheat I).....	27.93
Bread (Whole wheat II).....	27.08
Bread (Wheat flour I) .....	39.70
Bread (Wheat flour II).....	31.99
Corn cake (Maize).....	40.37

#### 4. ESTIMATION OF THE PENTOSANS AND HEMICELLULOSES BY DILUTE ACIDS.

After removing the more easily soluble constituents of the material as already described, there remains the somewhat insoluble substance incorporated in the cell walls and intimately associated with the true cellulose.

This woody or fibrous material is very far however from possessing a homogenous character, but consists of some of the most complex and least understood of the carbohydrate group, as well as some substances which cannot be regarded as carbohydrates at all.

Tollens regards the lignified cells as composed of three general classes of substances: cellulose, wood gum or pentosans, and bodies belonging undoubtedly to the aromatic group. This last is of non-carbohydrate nature. Of the first two, cellulose may be regarded as resistant to any of the reagents here proposed, while the wood gum or pentosan is easily hydrolyzed by dilute acids. In many materials other substances similar to the pentosans will occur, as for instance, galactan, mannan, dextran, even of substances of the nature of pectin, but all these behave like the pentosans to hydrolytic agents and yield specific sugars. Recent researches by Cross and Bevan throw much light upon the constitution of these non-cellulose materials. The hydrolyzable portions seem to be largely of the nature of pentosans or their derivatives.<sup>1</sup> The most rational treatment of the material at this stage would therefore seem to be such as would dissolve this group of similar substances and convert them into a form capable of ready estimation. For this purpose, treatment with dilute hydrochloric acid has been found preferable to any other.

The reagent was selected because, as shown by Counciler,<sup>2</sup> it possesses superior hydrolytic power to sulphuric acid towards these very substances. Repeated use of hydrochloric acid in this laboratory for the purposes of hydrolyzing large quantities of gums and similar materials has shown that its action is quicker and that fewer by-products result than when sulphuric acid is used.

A recent paper by Cross, Bevan and Smith,<sup>3</sup> suggests the use of one per cent. sulphuric acid for this purpose, and heating in an autoclave during thirty minutes at a pressure of three atmospheres. Their results do not indicate a greater degree of efficiency than the method here presented, while the operation would prove less convenient for many analysts.

With regard to the duration of treatment and the strength of

<sup>1</sup> *Chem. News*, 74, 175; *Ber. d. chem. Ges.*, 29, 1457.

<sup>2</sup> *Chem. Ztg.*, 16, 1719.

<sup>3</sup> *Ber. d. chem. Ges.*, 29, 1457.

acid to be employed, a systematic study has indicated that one hour's boiling under a reflux condenser with 100 cc. of one per cent. hydrochloric acid, gave the most satisfactory results. The accuracy of this conclusion was determined by ascertaining the conditions which yielded the largest amount of reducing sugar without appreciably diminishing the amount of crude fiber obtained at the close of the analysis, it being thought undesirable to increase the intensity of this reaction at the expense of the fiber. After one hour's boiling with the acid of the concentration mentioned, there remains in the material only very slight traces of soluble matters which could be converted into reducing sugars.<sup>1</sup>

In the absence of other bodies similar to the pentosans this method will undoubtedly furnish a quicker and more accurate method of determining the latter than the well known destructive distillation with strong hydrochloric acid and subsequent estimation of the furfural thus found.

As a factor for the reducing coefficient of the sugars thus formed, that of xylose has been chosen as probably representing the most common and most abundant sugar present under these conditions (one cc. Fehling's solution requires for complete reduction 0.004617 gram of xylose.)<sup>2</sup>

The equivalent of xylose in xylan as originally present in the material may be estimated after the manner of finding the equivalent of dextrose in starch, according to the proportion



PENTOSANS DISSOLVED BY BOILING WITH ONE PER CENT. HYDROCHLORIC ACID.

	Per cent.
Wheat I.....	4.54
Wheat II.....	4.37
Wheat flour I.....	0.00
Wheat flour II.....	0.00
Maize .....	5.14
Sugar beet (Fresh) .....	4.89
Hay.....	7.14
Bread (Whole wheat I).....	4.16
Bread (Whole wheat II).....	4.34
Bread (Wheat flour I).....	0.00
Bread (Wheat flour II).....	0.00
Corn cake (Maize).....	3.54

<sup>1</sup> Cross, Bevan and Beadle, This Journal, 18, 8, state that the residue from a successive treatment by boiling alcohol, dilute sodium hydroxide, and dilute hydrochloric acid is free from pentosans and all the more readily hydrolyzable constituents.

<sup>2</sup> *Am. Chem. J.*, 13, 73.

## 5. ESTIMATION OF CRUDE FIBER.

The residue from the preceding treatment still contains in addition to the actual fiber or cellulose a considerable amount of a substance not hydrolyzable to reducing sugars, by means of dilute acids, but which is readily soluble in dilute alkalies. This frequently forms a considerable proportion of the nitrogen-free extract. Repeated treatment of such alkaline solutions with dilute acids (after neutralizing the alkali) have failed to produce any considerable amount of reducing sugars. An investigation of the nature of this substance is now in progress, but there seems little ground at this time for regarding it as of the nature of a carbohydrate. It probably deserves separate classification as non-nitrogenous and non-carbohydrate in its nature.

The residue from treatment with dilute acid is therefore boiled under a reflux condenser for thirty minutes with 200 cc. of 1.25 per cent. sodium hydroxide, filtered, washed, dried, weighed, and ignited in the manner prescribed for the ordinary estimation of crude fiber.

Following are the results obtained in this way :

CRUDE FIBER RESULTING AFTER TREATMENT WITH BOILING ALCOHOL,  
COLD WATER, MALT EXTRACT, BOILING ONE PER CENT. HYDRO-  
CHLORIC ACID AND BOILING ONE AND ONE-FOURTH  
PER CENT. SODIUM HYDROXIDE.

	Per cent.
Wheat I.....	2.68
Wheat II.....	2.51
Wheat flour I.....	0.25
Wheat flour II.....	0.25
Maize .....	1.99
Sugar beet (Fresh) .....	1.00
Hay.....	34.34
Bread (Whole wheat I).....	2.70
Bread (Whole wheat II).....	2.02
Bread (Wheat flour I).....	0.34
Bread (Wheat flour II).....	0.17
Corn cake (Maize).....	2.22

The percentage of crude fiber obtained in this way will not be essentially different from the results obtained by the Weender method.

A better comprehension of the significance of these results

will be had from their collective presentation in the following table. From this it will be seen that in each material six, or in some cases, seven forms of carbohydrates have been quantitatively determined, the results showing at a glance the comparative value of the material for use either as a food or for technical purposes, as no other existent method of analysis could do. The sum of these various items constitute of course the total carbohydrates in the respective materials.

TABLE SHOWING THE RESPECTIVE PERCENTAGES OF DIFFERENT CARBOHYDRATES IN CERTAIN FOOD-STUFFS.

Material analyzed.	Sucrose. Per cent.	Invert sugar. Per cent.	Dextrin. Per cent.	Soluble starch. Per cent.	Normal starch. Per cent.	Pentosans. Per cent.	Crude fiber. Per cent.
Wheat I.....	0.52	0.08	0.27	0.00	30.94	4.54	2.68
Wheat II.....	0.72	0.00	0.41	0.00	30.36	4.37	2.51
Wheat flour I.....	0.18	0.00	0.90	0.00	46.19	0.00	0.25
Wheat flour II.....	0.20	0.00	1.06	0.00	34.04	0.00	0.25
Maize .....	9.27	0.00	0.32	0.00	42.50	5.14	1.99
Sugar beet (Fresh)....	8.38	0.07	0.35	0.00	0.00	4.89	1.00
Hay .....	2.53	0.00	1.18	0.00	7.49	7.18	34.34
Bread (Whole wheat I)	0.05	0.32	0.68	1.37	27.93	4.16	2.70
Bread (Whole wheat II)	0.06	0.37	0.23	2.36	27.08	4.34	2.02
Bread (Wheat flour I).	0.01	0.10	0.27	1.99	34.70	0.00	0.34
Bread (Wheat flour II)	0.15	0.38	0.91	1.74	31.99	0.00	0.17
Corn cake (Maize)....	0.16	0.19	0.00	2.80	40.37	3.54	2.22

In many cases it is believed that the total amount of carbohydrates thus definitely determined in food materials will be found to be appreciably less than the nitrogen-free extract estimated by difference. If subsequent research should justify this belief, the character of this non-carbohydrate and non-nitrogenous substance would remain to be determined. This question is now being investigated and for the present the writer desires to reserve the subject of inquiry to this laboratory.

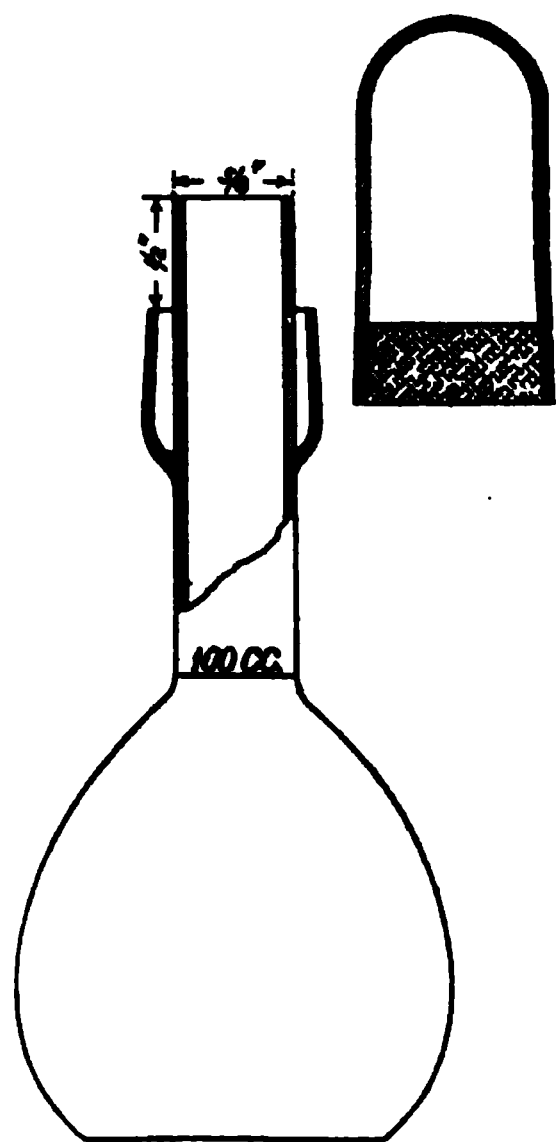
This outline is thought to present an analytical method superior to anything at present available for the estimation of carbohydrates in foods, although it cannot be regarded as in any sense perfected. It will have served its purpose if it shall suggest to others the necessity of something better and assist them in the search for it.

# A NEW CALIBRATED WEIGHING FLASK.

BY GEORGE L. HEATH.

Received January 8, 1897.

**A** FLASK has been designed by the writer which possesses some advantages over the ordinary graduated flasks in use. From the designs, Eimer and Amend, of New York, make very neat flasks, which may be illustrated by the accompanying diagram.



The drawing shows the upper part of the neck, as if half cut away, giving a sectional view of the stem, and annular cup surrounding it.

The outside of the cup is ground to fit the light glass cap which slips over it. (See sectional view of cap.)

The flask is especially adapted to weighing liquids, as, for instance, portions of standard ferric chloride solutions for titrations as recommended in Blair's Iron Analysis.

The solution may be kept some time without any change in weight, since the joint of cup and cap is as tight as in other glass stoppered bottles.

A little vaseline may be used, for the cap never comes in contact with the solution like an ordinary stopper.

This form of stopper cannot cement to the flask. After weighing and then mixing some solution, a portion may be poured off, and the little annular cup will retain any drop that might drip over the edge in pouring, and the cap, immediately replaced, prevents evaporation till the flask and remaining contents can be weighed.

In selecting ordinary graduated flasks to be fitted with such an annular cup and glass cap, those are preferably taken which have rather narrow necks, for the graduation of such is a little more accurate, and the cap, etc., may be smaller and neater in appearance, especially when applied to a large sized vessel.

The moderate expense necessary to fit flasks in this manner is the only disadvantage we have noted.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY.]

## THE VELOCITY OF THE REACTION BETWEEN FERROUS CHLORIDE, POTASSIUM CHLORATE AND HYDROCHLORIC ACID.

BY A. A. NOYES AND R. S. WASON.

Received January 12, 1897.

### I. PURPOSE OF THE INVESTIGATION.

THE velocity of the reaction between ferrous sulphate, potassium chlorate, and sulphuric acid was investigated many years ago by J. J. Hood.<sup>1</sup> The results of his experiments are briefly as follows: In the presence of an undetermined excess of sulphuric acid, the velocity of the reaction at any moment was found to be directly proportional, throughout each separate series of experiments, to the product of the concentrations of the ferrous sulphate and potassium chlorate. This was proved to be true not only in the series where these two substances were originally present in equivalent amounts, but also in those where one or the other of the two substances was present in excess. The author states, without presenting experimental results, that the same law was found to govern the reaction between ferrous chloride, potassium chlorate, and hydrochloric acid. He also studied the effect of acid on the former reaction, and showed that its velocity increased more rapidly than the increase in the concentration of the acid. He determined, furthermore, the relative influence of sulphuric and hydrochloric acids on the rate of the reaction, and also the effect of varying the temperature between the limits of 10° and 32°.

We have undertaken the investigation of the very similar reaction referred to in the title of this article with several objects in view: First, in order to confirm Hood's conclusion that the reaction is one of the second order with respect to the ferrous salt and the chlorate, by the far more reliable method<sup>2</sup> of varying the initial concentration and comparing the velocity constants of the different series. Second, in order to determine more definitely the influence of acid, especially hydrochloric acid, on the speed of the reaction: if found proportional to the concentration of the acid, the result would be of interest as furnishing a new

<sup>1</sup> *Phil. Mag.* (5), 6, 371; 8, 121; 20, 323.

<sup>2</sup> See Noyes: *Ztschr. phys. Chem.*, 18, 118.

example of a third order reaction; if not proportional, the velocity might prove, like that of the reaction between hydriodic and bromic acids,<sup>1</sup> to be proportional to the square or some other simple power of the concentration of the hydrogen ions. Third, in order to investigate within wider limits the effect of temperature on the velocity of the reaction, with a view of further confirming the remarkable laws which have lately been discovered in regard to the relation between temperature and reaction-velocity.

It seemed desirable, moreover, to undertake this investigation in spite of the extended experiments of Hood on the analogous sulphate reaction, by reason of the fact that, according to the Electrolytic Dissociation Theory, the molecular composition of the dissolved substances is much simpler in the case of the chlorides than in that of the sulphates; namely, at the concentration used in these experiments, hydrochloric acid is nearly completely dissociated, while sulphuric acid is dissociated only to a moderate extent, so that its degree of dissociation varies considerably with its concentration, which is therefore not proportional to the concentration of the hydrogen ions. Furthermore, ferrous sulphate is less dissociated than ferrous chloride; and ferric sulphate, which is a product of the reaction, is hydrolyzed to a greater extent than the corresponding chloride. A closer correspondence of the experimental results with simple empirical and theoretical formulas is therefore to be expected in the case of the chloride.

## 2. THE EXPERIMENTAL METHOD OF PROCEDURE.

The standard stock solutions employed in our investigation were a half-normal solution of ferrous chloride and one of potassium chlorate, a normal solution of hydrochloric acid, and an approximately tenth-normal solution of potassium permanganate.<sup>1</sup> The ferrous chloride solution was prepared by boiling strong hydrochloric acid with a large excess of pure iron wire, with a return cooler, as long as any action took place; the solution was then diluted until it became exactly half-normal, a standard potassium bichromate solution being used for this purpose. The

<sup>1</sup> Noyes: *Ztschr. phys. chem.*, 19, 599.

<sup>2</sup> The word normal is used throughout this article with reference to the oxidizing power of the substance.



ferrous chloride solution was kept under a pressure of carbon dioxide, in order to prevent its oxidation. A chlorine determination made in it showed that it was almost perfectly neutral. The half-normal potassium chlorate solution was made by dissolving 10.21 grams of the recrystallized commercial salt in one liter of water. The hydrochloric acid solution was prepared by diluting the chemically pure acid, pure calcium carbonate being used for its standardization. The permanganate solution used was standardized against the ferrous chloride solution, and was found to be 0.1011 normal; 25.00 cc. of the ferrous solution, measured after it was diluted to a tenth-normal concentration, therefore required 24.72 cc. of this permanganate solution.

In carrying out the velocity experiments, a mixture of the reacting substances consisting of 250 or 500 cc. was made up by means of pipettes from the stock solutions and from freshly boiled distilled water in glass-stoppered bottles from which the air had been displaced by carbon dioxide. The appropriate amounts of water, ferrous chloride solution, and hydrochloric acid, were first placed in the bottles, which were then put into a large water thermostat provided with an efficient stirrer. After the mixture had attained the temperature of the bath, the proper amount (50 or 100 cc.) of the chlorate solution previously brought to the same temperature, was added from a rapidly delivering pipette, the time noted, and the mixture instantly shaken. After suitable intervals, portions of twenty-five or fifty cc. were removed, and run into 200–300 cc. of cold, boiled water containing about one gram of manganous sulphate and small quantities of sulphuric acid and sodium phosphate; this solution was then immediately titrated with the permanganate. It is known<sup>1</sup> that under these conditions the permanganate process furnishes accurate results, even though chlorides are present; and in our own experiments no difficulty was found in getting a sharp endpoint.

The temperature of the thermostat was kept constant in all cases within 0.1° C., and was 20° unless otherwise mentioned.

### 3. EXPERIMENTAL RESULTS ON THE EFFECT OF THE CONCENTRATION OF THE REACTING SUBSTANCES.

The three reacting substances were brought together in nine

<sup>1</sup> Zimmermann: *Ber. d. chem. Ges.*, 14, 779; Reinhardt: *Chem. Ztg.*, 13, 323; Mixer and DuBois: *This Journal*, 17, 406.

different proportions, in order to establish with certainty the order of the reaction, and to show the effect of each substance separately on its velocity. In the first five series the concentrations of the ferrous chloride and potassium chlorate were kept constant, and that of the hydrochloric was varied. In five of the series, on the other hand, the amount of acid present was constant, and the concentrations of the other two substances were variable.

Check determinations were made in every case. The results of all these experiments are presented in the table below. The values in the column headed  $t$  are the times in minutes counted from the moment of mixing. Those in the columns headed  $x_1$  and  $x_2$  are the number of cubic centimeters of the permanganate solution corresponding to the amount of ferrous salt already oxidized at the time  $t$  in the two duplicate experiments. The values of  $x$  are the means of these two quantities. The values of  $A - x$  represent the number of cubic centimeters corresponding to the unoxidized ferrous salt present at the time  $t$ . The initial value of ferrous salt in terms of the permanganate—that is, the value of  $A$ —is 24.72 in all the series except Nos. 7 and 9, and 49.44 in the case of these two series.<sup>1</sup> The columns headed  $10^6 C_2$  and  $10^7 C_3$  contain the calculated values of the velocity-constants of the second and third orders respectively. The values of  $C_1$  are those of the constant in the differential equation :

$$\frac{dx}{dt} = C_1(A - x)(B - x),$$

where  $A$  and  $B$  represent the initial quantities of ferrous chloride and potassium chlorate, and  $x$  the amount changed over at the time  $t$ , and where the variation in the concentration of the hydrochloric acid is disregarded. The values of  $C_1$  are those of the constant in the equation :

$$\frac{dx}{dt} = C_1(A - x)(B - x)(C - x),$$

which states that the velocity of the reaction is directly proportional to the concentration of each of the three reacting substances. For the integrated forms of this equation by which the numerical calculations were made in the different cases, we refer

<sup>1</sup> For twenty-five cc. of the reaction-mixture were titrated in series Nos. 1 to 5, and in No. 9, and fifty cc. in the other series (Nos. 6 to 8).

to the article of Fuhrmann.<sup>1</sup> All of these constants are expressed in the same arbitrary units, those corresponding to the number of cubic centimeters of permanganate required for the titration. If the values of  $A$ ,  $B$ ,  $C$ , and  $x$  were expressed in gram-equivalents per liter, the values of  $C$ , would be 247.2 times, and the values of  $C$ , 61120 times as great as those here given. We mention this fact, for we think it unfortunate that authors in presenting the results of investigations on the velocity of reactions so often neglect to determine, or at any rate to state, the factor by which their arbitrary reaction-constants can be reduced to an absolute standard.

TABLE I.

Series No.	Normal concentration of			$t$ .	$x_1$ .	$x_2$ .	$x$ .	$A - x$ .	$10^6 C_2$ .	$10^7 C_2$ .
	FeCl <sub>3</sub> .	KClO <sub>3</sub> .	HCl.							
1	0.1	0.1	0.0	15	0.00	0.00	0.00	24.72	...	...
				45	0.03	0.01	0.02	24.70	...	...
				100	0.08	0.05	0.06	24.66	...	...
				250	0.55	0.48	0.51	24.21	...	...
2	0.1	0.1	0.1	5	1.22	1.14	1.19	23.53	408	171
				15	3.04	3.00	3.02	21.70	375	162
				35	5.79	5.97	5.88	18.85	360	168
				60	8.24	7.97	8.12	16.60	331	166
				110	11.26	11.07	11.17	13.55	303	173
				170	13.05	12.96	12.98	11.74	264	165
3	0.1	0.1	0.2	5	2.50	2.42	2.46	22.28	886	189
				15	5.42	5.40	5.41	19.31	756	162
				35	9.60	9.82	9.70	15.08	746	171
				60	12.25	12.35	12.30	12.40	670	160
				107	15.27	15.40	15.32	9.40	616	158
				167	17.54	17.67	17.62	7.10	600	136
4	0.1	0.1	0.3	5	3.37	3.22	3.32	21.40	1250	174
				12	6.57	6.42	6.49	18.23	1200	170
				22	9.56	9.47	9.52	15.20	1150	168
				35	12.27	12.22	12.25	12.47	1130	174
				55	14.47	14.60	14.54	10.18	1050	177
				85	16.97	16.97	16.97	7.75	1030	166
5	0.1	0.1	0.5	1	1.20	1.12	1.16	23.56	2000	163
				3	3.44	3.52	3.48	21.24	2210	181
				7	7.00	6.92	6.96	17.76	2240	189
				12	9.72	9.72	9.72	15.00	2180	185
				22	13.28	13.22	13.24	11.48	2120	185
				37	16.10	16.14	16.12	8.60	2050	182

<sup>1</sup> *Ztschr. phys. Chem.*, 4, 89.

Series No.	Normal concentration of			<i>t</i> .	$x_1$ .	$x_2$ .	$x$ .	$A-x$ .	$10^6 C_2$ .	$10^7 C_3$ .
	FeCl <sub>2</sub> .	KClO <sub>3</sub> .	HCl.							
6	0.05	0.05	0.2	5	1.12	1.08	1.10	23.62	708	153
				15	3.22	3.14	3.18	21.54	796	164
				50	7.97	8.10	8.02	16.70	776	165
				100	11.84	11.89	11.86	12.86	768	162
				160	14.62	14.67	14.65	10.07	738	165
				250	16.82	16.97	16.90	7.82	700	160
7	0.1	0.05	0.2	5	2.14	2.49	2.30	47.14	788	157
				12	4.72	4.87	4.30	44.64	790	160
				40	11.81	11.64	11.74	37.70	744	164
				70	15.54	15.51	15.53	33.91	708	161
				110	18.44	18.52	18.49	30.95	668	154
				170	21.10	20.94	21.04	28.40	642	149
8	0.05	0.1	0.2	5	2.02	2.27	2.17	22.55	762	161
				12	4.92	5.07	5.00	19.72	804	166
				22	8.02	8.10	8.07	16.65	798	169
				40	11.92	11.92	11.92	12.80	762	168
				70	15.92	15.86	15.89	8.83	740	160
				110	18.82	18.87	18.82	5.90	700	162
9	0.2	0.2	0.2	1	1.94	1.94	1.94	47.50	830	170
				2	3.72	3.76	3.74	45.70	830	175
				4	6.71	6.77	6.74	42.70	800	174
				7	10.29	10.24	10.26	39.20	749	170
				15	16.49	16.71	16.61	32.83	682	173
				25	21.32	21.26	21.29	28.15	612	170

#### 4. DISCUSSION OF THE RESULTS ON THE EFFECT OF THE CONCENTRATION OF THE REACTING SUBSTANCES.

The first series of experiments presented above clearly shows that in neutral solution the reaction does not take place to an appreciable extent. The very slight decrease in the concentration of the ferrous salt, amounting only to a quarter of a per cent. in 100 minutes and to two per cent. in 250 minutes, may well be due to oxidation by the air or to the presence of a small quantity of acid in the ferrous chloride solution.

Attention may next be directed to the fact that, in the experiments in which the acid was present in large excess, especially in Series No. 5, the values of  $C_2$  are nearly constant, thus confirming Hood's conclusion that the velocity of the reaction under such circumstances is directly proportional to the product of the concentrations of the ferrous salt and of the chlorate.

The order of the reaction and the effect of each substance on

its velocity, is, however, best determined by applying to the results as a whole the two distinct methods available for this purpose.

The first of these methods is the one most commonly employed. It consists in determining which order of constants shows the smallest variations throughout each *separate* series of experiments. Now, a brief inspection of the foregoing table suffices to show that, in all the series except those where a large excess of the acid was present, the values of  $C_1$  show a continuous decrease as the reaction progresses; that the value of  $C_2$ , on the other hand, in every case remains practically constant, or exhibits only irregular variations plainly arising from experimental errors. Judged by this method, the reaction is therefore one of the third order.

The second method of determining the order of reactions was first employed by van't Hoff,<sup>1</sup> and its importance was later emphasized by the experiments of Noyes and Scott.<sup>2</sup> In the form used by the latter investigators it consists in determining which order of constants has most nearly the same value in independent series of experiments in which the initial concentrations are made widely different from one another. This method is much more reliable than the first one by reason of the fact that the influence of disturbing causes, such as the effect of the products of the reaction on its velocity, becomes insignificant in comparison with the much greater effect of the large changes in the initial concentrations. In order to show more clearly the result of the application of this second method to the reaction here considered, we have prepared the following table, in which are brought together the comparable values of the two orders of constants derived from the eight series of experiments; namely, the mean values of  $C_1$  and the values of  $C_2$  corresponding to that stage of the reaction at which one-half of the iron is oxidized.

TABLE II.

Series No.	Normal concentration of			$10^3 C_1$	$10^7 C_2$
	FeCl <sub>2</sub>	KClO <sub>3</sub>	HCl		
2	0.1	0.1	0.1	243	168
3	0.1	0.1	0.2	670	163
4	0.1	0.1	0.3	1130	172
5	0.1	0.1	0.5	2130	184
6	0.05	0.05	0.2	763	163
7	0.1	0.05	0.2	739	157
8	0.05	0.1	0.2	760	164
9	0.2	0.2	0.2	727	172

<sup>1</sup> *Études de dynamique chimique.*<sup>2</sup> *Ztschr. phys. Chem.*, 18, 118.

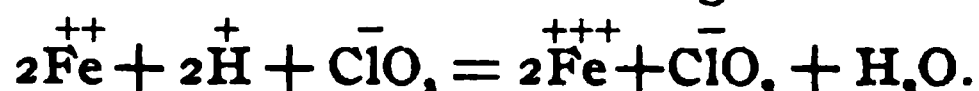
It is seen that the values of  $C_1$  are approximately the same in all eight series of experiments, conclusively proving that the reaction is one of the third order, and that its velocity is proportional to the concentration of each of the reacting substances. The values of  $C_2$  increase as the concentration of the acid increases, but are, like those of  $C_1$ , approximately constant in the last four series of experiments, in all of which the same excess of acid was present, showing that the reaction is one of the second order in the presence of an excess of acid.

These experiments furnish the first satisfactory example of a reaction of the third order in which three distinct substances are involved.

It is worth while to consider briefly the question of the theoretical significance of the fact that this reaction is one of the third order. The following equation expresses the change which, according to the Electrolytic Dissociation Theory, takes place in the molecular composition of the substances in solution :



It is seen that no less than thirteen molecules are involved in this reaction. It is, however, highly probable that the reduction of the chlorate takes place in three separate stages, and that it is only the first one of these which requires an appreciable time for its completion ;<sup>1</sup> in which case the reaction whose velocity is measured would be the following one :



But even in this reaction five molecules participate ; and it would, therefore, be expected, in accordance with kinetic and thermo-dynamical considerations, that the reaction would be one of the fifth order, or one of the third order in presence of the excess of acid.

The only kinetic explanation of the actual order of the reaction that we are able to suggest is that the ferrous ions are diatomic (namely of the formula  $\overset{++++}{[\text{Fe}_2]}$ , and that the hydrogen ions in the first instance act catalytically. The reaction whose velocity is measured would then be :  $\overset{++++}{[\text{Fe}_2]} + \overset{-}{\text{ClO}_3} = \overset{++++}{[\text{Fe}_2\text{O}]} + \overset{-}{\text{ClO}_2}$ , or  $\overset{++++}{[\text{Fe}_2]} + \overset{-}{\text{ClO}_3} + \text{H}_2\text{O} = 2\overset{+}{\text{FeOH}} + \overset{-}{\text{ClO}_2}$ , the basic ferric ion

<sup>1</sup> Compare Noyes : *Ztschr. phys. Chem.*, 19, 599.



Series No.	Temperature.	<i>t</i> .	<i>x</i> <sub>1</sub> .	<i>x</i> <sub>2</sub> .	<i>x</i> .	<i>A</i> — <i>x</i> .	10 <sup>4</sup> <i>C</i> <sub>g</sub> .	10 <sup>7</sup> <i>C</i> <sub>g</sub> .
12	30°	5	2.45	2.35	2.40	22.50	856	357
		10	4.50	4.55	4.52	20.38	891	387
		18	6.70	6.72	6.70	18.20	821	390
		32	9.52	9.50	9.50	15.40	774	406
		55	12.07	12.05	12.06	12.84	703	404
		95	14.65	14.70	14.68	10.22	606	418
13	40°	5	5.30	5.15	5.22	19.68	2130	971
		9	7.57	7.61	7.59	17.31	1950	954
		16	10.50	10.42	10.46	14.44	1810	992
		30	13.40	13.59	13.50	11.40	1580	1010
		50	15.65	15.60	15.62	9.28	1350	990
		80	17.48	17.50	17.49	7.41	1180	1030
14	50°	1	2.55	2.40	2.48	22.42	4440	1970
		3	6.18	6.25	6.22	18.68	4480	2050
		6	9.55	9.38	9.46	15.44	4100	2140
		11	12.62	12.65	12.64	12.26	3760	2290
		20	15.38	15.42	15.40	9.50	3250	2370
		30	17.00	16.97	16.98	7.92	2150	2390

## 6. DISCUSSION OF THE RESULTS ON THE EFFECT OF TEMPERATURE.

As was first shown by van't Hoff,<sup>1</sup> it follows from the laws of thermodynamics that the following relation must exist between the absolute temperature *T*, the heat effect *q* accompanying the reaction, and the velocity-constants, *k'* and *k''*, of the two opposing reactions which are considered to be in equilibrium with one another:

$$\frac{d \log_{\cdot} k'}{dT} - \frac{d \log_{\cdot} k''}{dT} = \frac{q}{2T^2}.$$

Van't Hoff adds that, although this equation does not give the desired relation between temperature and the velocity constants of the *separate* reactions, it shows nevertheless that the relation has the following form:

$$\frac{d \log_{\cdot} k}{dT} = \frac{A}{T^2} + B.$$

It is to be noted, moreover, that in this equation *A* is a quantity which, like *q* in the preceding one, will, in general, probably vary but little with the temperature, and that *B* is a quantity which must have the same numerical value for the two opposed

<sup>1</sup> Etudes de dynamique chimique, p. 115.



reactions at any temperature at which they may be compared, for only in that case would this term disappear in the preceding equilibrium equation. This fact in regard to the quantity  $B$  makes it seem probable that its value is zero. At any rate, this is the simplest assumption that can be made in regard to it, and the one whose validity it is first natural to test by a comparison with the facts. Integrating then the differential equation between the limits  $T_1$  and  $T_2$  (to which correspond the velocity constants  $k_1$  and  $k_2$ ), under the assumptions that  $B = 0$ , and that  $A$  does not vary with the temperature, we get :

$$\log. \frac{k_1}{k_2} = \frac{T_1 - T_2}{T_1 T_2}.$$

Now, it has been shown by Arrhenius<sup>1</sup> that this equation does in fact satisfactorily represent the relation between temperature and velocity-constants in the case of five different reactions. In the case of two other reactions considerable deviations from the formula were found to exist, but these were attributed to experimental errors arising from the high temperatures employed.

In order to determine whether our results are in accord with this formula, we have calculated the ratios ( $k_1 : k_2$ ) of the mean values of  $C$ , for each successive pair of temperatures, and from these ratios we have calculated the constant  $A$  in the above equation, and have brought the results together in the following table :

TABLE IV.

Series No.	Temperature.	$10^7 C$ , or $k$ .	$k_1 : k_2$ .	$A$ .
10	0	22.7	2.75	7820
11	10	62.4	2.68	8180
12	20	167.0	2.36	7620
13	30	394.0	2.52	8760
14	40	992.0	2.22	8070
15	50	2200.0	...	....

It will be seen that the values of  $A$  show only irregular variations, not a progressive one, and therefore the equation is correct within the experimental error. It is to be noted that the simpler equation :

$$\log. \frac{k_1}{k_2} = B(T_1 - T_2)$$

(where  $B$  is a constant) corresponding to the relation ( $k = ab^t$ )

<sup>1</sup> *Ztschr. phys. Chem.*, 4, 226.

employed by Berthelot in connection with his esterification experiments, would be a less satisfactory expression of the results; for this equation would require that the values of the ratios  $k_1 : k_2$  should be constant at all temperatures, instead of slowly decreasing with rising temperature, as the previous equation required, as is in fact the case.

Another remarkable conclusion to which the study of the effect of temperature on the velocity of reactions has led, is that temperature apparently accelerates all chemical changes in approximately the same ratio. In other words, the values of the ratios  $k_1 : k_2$  for equal differences of temperature are of the same order of magnitude for all the various reactions investigated, although these reactions differ from one another in character as widely as possible. For a ten-degree interval the average value of  $k_1 : k_2$  is about 2.8, the separate values varying from 2.0 to 3.6.<sup>1</sup> We wish now only to call attention to the fact that the reaction here considered is another example of this principle, the value of the ratio  $k_1 : k_2$  being about 2.7 for the two lower temperature-intervals.

#### 7. SUMMARY.

This investigation has proved that the reaction between ferrous chloride, potassium chlorate, and hydrochloric acid is a reaction of the third order, its velocity being directly proportional to the concentration of each of the three substances. This conclusion is based not only on a consideration of the variations of the constants of the individual series, but also on the far more reliable comparison of the constants of different series of experiments made with varied initial concentrations.

It has also been proved that the effect of temperature on its velocity is expressed by van't Hoff's theoretical equation :

$$\frac{T_1 T_2}{T_1 - T_2} \log_{10} \frac{k_1}{k_2} = A \text{ (a constant),}$$

a formula whose applicability to several reactions had already been demonstrated by Arrhenius.

Finally, our experiments have shown that this reaction furnishes another confirmation of the empirical principle that the influence of temperature on the velocity of all reactions is of the same order of magnitude.

<sup>1</sup> For a summary of the results, see van't Hoff-Cohen: *Studien zur chemischen Dynamik*, p. 129.

## DISCUSSION.

*Mr. Hazen:* There is a question, different, although somewhat similar, to that presented in the paper, which has been interesting me of late; that is, the speed with which ferrous iron in waters is oxidized to the ferric state. Ferrous iron in solution in public water supplies is a very troublesome substance. In order to get rid of it, it has to be first converted into ferric iron which can be readily removed by filtration. I have made some experiments with this removal during the past year in connection with a plant for removing iron from municipal supply, installed under our advice.

After the water was aerated and had been standing in a basin for several hours, apparently every bit of the iron was in the ferrous condition, no oxidation whatever having taken place, although the water was thoroughly aerated. The effluent from the filtration of this water was entirely free from iron, and the iron removed from the water was deposited on top of the filtering sand. It was not in the upper layers of the sand but actually on top of it.

It seems to me from this that the oxidation of the iron took place practically instantaneously and at the time when the water came in contact with the surface layer of the filter. There was no oxidation up to that time, and the oxidation then must have been complete, as no iron was deposited below or came through in the effluent. I have noticed in other cases that when the oxidation takes place gradually, the removal of iron is never complete, a small quantity remaining unoxidized in solution; but if the oxidation can be brought about at once, the action is complete and every trace of the iron is removed. In the above mentioned case, the oxidation of the iron must have been due to the water coming in contact with the ferric hydroxide already oxidized and precipitated, or to the friction and agitation of the water in getting into the filter; which, of course, introduces an entirely different condition of affairs from that of quiet standing water.

*Dr. Loeb:* In the equation, as written by Dr. Noyes, there seems to me to be one little matter left out of account, and that is as to the chlorine ions from the hydrochloric acid. Of course the hydrogen is being taken away with a part of the chlorine, the

hydrogen being oxidized, but at the same time fresh chlorine is being generated by the reduction of potassium chlorate to potassium chloride, and it seems to me, therefore, that that ought to be taken into account. I want to ask whether some neutral salt had been added in this reaction, say potassium chloride in definite quantities to see whether the influence of chlorine not in the shape of acid should be taken into account. It seems to me, if it is proved that potassium chloride is of absolutely no effect, that a question would arise, whether the influence of chloric acid, or, say,  $\text{ClO}_3$ , as an ion as compared with  $\text{Cl}$  as an ion will produce the difference or not. The other question I want to ask is this: I see an equation, the actual ratio between zero and ten. In some experiments I have made, with the same reaction I found that at zero and at three or four degrees I was unable to produce action at all; that is, if I took the proportion given here at zero degrees I had no reaction whatever. It would be interesting to know whether Dr. Noyes obtained a reaction at zero or whether the value is obtained by extrapolation.

*Dr. Noyes:* Replying to the first question I would say that no experiments were made on the effect of potassium chloride on the velocity of the reaction; nor, as far as the reliability of the conclusions are concerned, are they necessary. For the effect of the reaction products is eliminated by the comparison of the constants of the independent series.

In regard to the experiments at zero degree, I would say that the temperature was kept at that point as nearly as possible by adding to the water in the thermostat a very considerable quantity of ice. It is probable, as is usual in such cases, that radiation raised the temperature a little above zero; I suppose it may have been one or two-tenths of a degree above zero, perhaps. But as the column of ratios shows, there was nothing at all abnormal in the results at zero degree.

*President Dudley:* It has seemed to me that the field opened here by Dr. Noyes has a very remarkable and wide extended application in the commercial process for making steel, which we hope to see this afternoon. Some years ago I had somewhat of a contest with the manufacturers over the question of the quality of the metal used for making rails. To make a

very long story short, the point I was trying to reach was to get a softer, tougher steel for rails than the steel maker wanted to make. The final answer to me was, "We cannot make a soft, tough steel as fast as we can make a hard or more brittle steel." Part of this result was due to mechanical characteristics, that is to say, the rolling of a harder, higher carbon steel is easier, since its melting-point is lower, and it softens more under heat. But, and the point I want to bring out is, the amount of the final additions, as they are called in the steel trade, that is of the spiegel and ferromanganese added at the end of the blow to remove the oxides that are formed, is considerably greater when you make a hard steel than when you make a soft steel. Now, I think it is perfectly clear that if you add to a bath of metal, after the blow is finished—which is in reality a substance containing a good deal of metallic iron and a good deal of oxide of iron—if you add say, in one case, 500 pounds of melted spiegel, and in another case 1000 pounds, the reaction will take place more rapidly in the second case. In reality therefore, the question of the speed of the reaction, which results in freeing the bath of metal from the oxide, is a very live and important question commercially, and I am only sorry to have to tell you that the steel people were a little stronger than I was, and consequently they are making steel about as they have a mind to, and getting out the oxide, we hope, but fear that they do not.

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[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY. NO. 21.]

## THE OXIDES OF TUNGSTEN.<sup>1</sup>

BY EN. D. DESI.

Received January 21, 1897.

WHILE engaged in re-determining the atomic mass of tungsten, by reduction of its trioxide in a current of hydrogen, the writer carefully observed the color changes taking place in the oxide as the temperature varied.

When studying the literature of this metal, no precise information was found about the bodies formed during the reduction, as was expected. Although a great many compounds of tungsten have been investigated, those of the metal with oxygen have

<sup>1</sup> From author's thesis presented to the University of Geneva, Switzerland, for the degree of Doctor in Science.

been entirely neglected. The few recorded observations relate solely to the results of qualitative experiments.

As most of the oxides of the other elements of group VI of the periodic system, as  $\text{CrO}$ ,  $\text{Cr}_2\text{O}_3$ ,  $\text{Cr}_3\text{O}_8$ ,  $\text{CrO}_2$ ,  $\text{CrO}_3$ ;  $\text{MoO}$ ,  $\text{Mo}_2\text{O}_3$ ,  $\text{Mo}_3\text{O}_8$ ,  $\text{Mo}_4\text{O}_{11}$ ,  $\text{Mo}_5\text{O}_{15}$ ,  $\text{MoO}_3$ ;  $\text{UO}$ ,  $\text{U}_2\text{O}_3$ ,  $\text{U}_3\text{O}_8$ ,  $\text{U}_4\text{O}_{10}$ ,  $\text{U}_5\text{O}_{15}$ ,  $\text{U}_6\text{O}_{18}$ , are well known and defined, the study of the oxides of tungsten was important.

The well-determined oxides of the metal are :

1. *Tungstic Acid*,  $\text{WO}_3$ , obtained by treating one of the minerals with aqua regia, or by treating a tungstate with an acid, or by igniting the metal in the presence of air.

2. *The Blue Oxide*,  $\text{W}_2\text{O}_7 = \text{WO}_3 \cdot \text{WO}_3$ , obtained by reducing the trioxide at a low temperature with hydrogen. Care must be taken not to heat above the formation of traces of water. In this way Malagutti<sup>1</sup> obtained a body of constant composition. It is also prepared by treating a soluble tungstate with hydrochloric acid and tin. The liquid takes on a beautiful deep blue color, due probably to the solution of the blue oxide in the hydrochloric acid.

3. *Tungsten Dioxide*,  $\text{WO}_2$ , a brown substance obtained by heating the trioxide to a red heat in a current of hydrogen, or by treating a soluble tungstate with hydrochloric acid and zinc. The dioxide formed in this way is very unstable; it rapidly oxidizes to tungstic acid.

As tungsten has many properties in common with the other elements of group VI, and especially with molybdenum, it should also form intermediary oxides.

Muthmann<sup>2</sup> has made interesting observations upon the oxides of molybdenum. He succeeded in finding definite methods for preparing them, as well as for determining their composition. In the course of the present work the writer will return to this subject.

#### PREPARATION OF TUNGSTIC ACID.

Commercial tungstic acid is a product of very dubious purity, even that of the leading manufacturers, marked C. P., invariably contains molybdic acid.

It seemed to me to be of the utmost importance to use in my

<sup>1</sup> *Ann. Chem.* (Liebig), 9, 273.

<sup>2</sup> *Ann. Chem.* (Liebig), 222, 108.

researches the purest possible material, so as to be perfectly sure that the reactions obtained are due solely to tungsten.

The preparation of chemically pure tungstic acid is a long and tedious operation which need not be described here, as it has already been outlined in detail by Smith and Desi.<sup>1</sup>

## OXIDES OF TUNGSTEN.

### I.

Muthmann<sup>2</sup> obtained molybdenum dioxide ( $\text{MoO}_2$ ) in beautiful violet crystals by heating the following mixture for several hours :

	Grams.
Ammonium molybdate.....	8
Boric acid .....	7
Molybdic acid.....	7
Fused potassium carbonate.....	24

On account of the great analogy between tungsten and molybdenum, it was thought that tungsten dioxide could be obtained by using the same method. A similar mixture was accordingly made, taking tungsten salts instead of molybdenum, and fusing in a covered platinum crucible for three hours. The result was a porous, white mass, and at the bottom of the crucible a very small quantity of a brown substance, insoluble in water or acids. When this was ignited in a porcelain crucible, with access of air, it did not change in appearance nor in weight.

The platinum crucible was badly corroded and a second experiment resulted in several holes ; a nickel crucible did not fare better.

The quantity of the brown substance was too small to allow of investigating its composition.

As satisfactory results could not be obtained with metal crucibles, the experiment was tried in a smooth Battersea crucible, using the following mixture :

	Grams.
Ammonium tungstate.....	9
Tungstic acid .....	7
Fused potassium carbonate.....	21
Boric acid.....	7

This mixture was heated in a wind furnace until a quiet fusion

<sup>1</sup>*J. Franklin Inst.*, 139, 290.

<sup>2</sup>*Ann. Chem.* (Liebig), 228, 116.

set in. After thorough cooling the crucible was broken in halves; beautiful light green crystals were found, resembling ammonium chloride in structure. After a few hours exposure to the air they became white.

Treated with water they broke down into an insoluble, amorphous, white substance free from boron, and into a soluble body. The latter, when acted upon with hydrochloric acid, became yellow in color, but when heated regained its former white color. The aqueous solution was concentrated on the water-bath; during this operation a point was reached, when a very viscous liquid was obtained, which could not be evaporated to dryness. This is one of the properties of a large number of double salts of boric and tungstic acids.

Diluting this viscous liquid with a few drops of water, it was placed in a vacuum desiccator, over sulphuric acid. After a week small crystals appeared, and a little later beautiful, hexagonal, perfectly developed prisms, soluble with difficulty in water. Besides these well-developed crystals, a white, amorphous powder separated, very soluble in water. The crystals were separated from the amorphous substance, dissolved in water and the solution placed in a vacuum desiccator. This operation was repeated several times, but the white, amorphous substance appeared every time, showing that the crystalline substance had broken down into two bodies, both containing tungsten, boron, and potassium.

The object being to investigate the oxides of tungsten, the study of these two bodies was not continued any further.

## II.

### ACTION OF SULPHURIC ACID UPON METALLIC TUNGSTEN AT THE ORDINARY ATMOSPHERIC PRESSURE.

In most of our chemical treatises the statement is made that metallic tungsten is not acted upon by sulphuric acid, or at least very slightly. The writer's experience demonstrates the contrary, for metallic tungsten is readily attacked by concentrated sulphuric acid at a temperature of  $200^{\circ}$  C. It is not possible, however, to dissolve it completely, even in the boiling acid. In this respect it differs from molybdenum, which is readily dissolved in concentrated sulphuric acid far below  $200^{\circ}$  C.



Metallic tungsten and thirty-five cc. of concentrated sulphuric acid were introduced into a small flask. Sufficient heat was applied to maintain a quiet evolution of sulphurous acid, showing thus, that a reduction took place and a blue substance was formed. As soon as sulphurous acid ceased to be evolved, heating was stopped.

Part of the blue substance was suspended in the liquid, subsiding after two or three days and then beginning to oxidize to tungstic acid. The clear, colorless, supernatant acid liquid, when treated with water, gave a precipitate of pure, yellow tungsten trioxide. On this account the dark blue substance in the flask was not washed with water but with alcohol and then ether, preventing, as much as possible, contact with the air as long as it was not perfectly dry.

In the subsequent experiments the heating, washing, and drying were made in an atmosphere of carbon dioxide.

The blue substance, once dried, is very stable. It precipitates metallic silver from a solution of silver nitrate and is readily oxidized to tungsten trioxide when ignited. Treated with ammonia, a gray metallic powder is formed which, according to analyses, is metallic tungsten.

0.1265 gram gray substance gave 0.1588 gram tungsten trioxide, equal to 0.1259 gram tungsten, or 99.53 per cent. tungsten.

The ammoniacal liquid, treated with hydrochloric acid, deposited yellow tungstic acid.

Several ignitions of the blue substance to tungsten trioxide, gave an average of 92.08 per cent. tungsten, corresponding well with the requirements of the formula of the monoxide of tungsten,  $WO$ , containing theoretically ninety-two per cent. tungsten.

*Experiment 1.*—0.0957 gram blue substance gave 0.1114 gram tungsten trioxide, or 0.0883 gram tungsten, or 92.25 per cent. tungsten.

*Experiment 2.*—0.1923 gram blue substance gave 0.2232 gram tungsten trioxide, or 0.1770 gram tungsten, or 92.03 per cent. tungsten.

*Experiment 3.*—0.2835 gram blue substance gave 0.3292 gram tungsten trioxide, or 0.2611 gram tungsten, or 92.02 per cent. tungsten.

Having determined the percentages of the tungsten, it was thought that a determination of the oxygen would be still more convincing. A weighed quantity of the blue substance was accordingly reduced in a current of hydrogen, the water from there-duction being collected in a weighed U-tube filled with freshly cal-cined calcium chloride.

*Experiment 1.*—0.5588 gram blue substance gave 0.0498 gram water, or 0.0437 gram oxygen, or 7.02 per cent. oxygen, thus proving conclusively that the blue substance is the *monoxide of tungsten*.

When we consider the decomposition of the monoxide of tung-sten by ammonia into metallic tungsten and a soluble tungstate, we must come to the conclusion that tungsten monoxide,  $WO$ , is not formed by the union of only one atom of tungsten and one atom of oxygen, but must be more complicated, perhaps  $W_2O.WO_3$ , which would correspond to tungstous acid.

The clear, colorless sulphuric acid solution obtained from the treatment of metallic tungsten with concentrated sulphuric acid, upon addition of water, precipitates yellow tungstic acid without passing first through the green and blue stages of oxidation. Evaporated in a platinum dish, it soon takes a dark brown color, almost black, and becomes very viscous; if water is added, a brown flocculent, very rapidly oxidizable precipitate is formed. On trying to filter, it oxidized very rapidly, so that it was impos-sible to obtain a homogeneous mass.

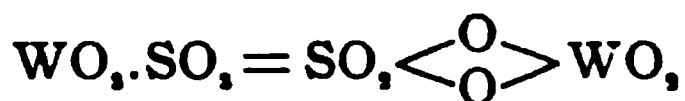
The color and behavior of this precipitate leads me to the supposition that it is *tungsten dioxide*, which shows the same properties when prepared in the wet way.

If we continue to evaporate to dryness, a brilliant, black, amorphous, very hygroscopic residue is left, which can be quite strongly heated, without any apparent change.

Several attempts were made to prepare a larger quantity of this black substance, but being very light, the greatest part is car-ried off by the heavy sulphuric acid fumes, very little remaining in the dish, not enough to make an analysis.

To determine the state of oxidation of the tungsten in the sul-phuric acid solution, ten cc. of it were added to 190 cc. of stand-ard potassium permanganate. Tungstic acid was precipitated; and titrating with a ferrous salt, almost no change was observed

in the standard of the permanganate, the difference being due only to the dilution. This means that the tungsten is in the sulphuric acid solution in its highest state of oxidation, and that it forms with sulphuric acid, like molybdenum, the anhydride of the sulphotungstic acid



which differs from that of molybdenum by its stability; that of molybdenum soon begins to take on a greenish color, indicating a reduction.

The formation of the sulphotungstic anhydride is also analogous to the combination of uranyl ( $\text{UO}_2$ ) with acid radicals, as  $\text{UO}_2 \cdot \text{SO}_3$ , etc.

If instead of treating tungsten with concentrated sulphuric acid at a low temperature, it be heated to the boiling-point of the acid, the evolution of sulphurous acid is violent, and two different substances will be seen floating in the liquid, one blue and the other white, settling down when the reaction is completed. These two substances were separated with great difficulty by an operation similar to "panning" with alcohol, then washing with ether and drying in an atmosphere of carbon dioxide.

Tungsten was determined in the greenish-blue substance by ignition and weighing of the resulting tungstic acid.

*Experiment 1.*—0.4796 gram greenish-blue substance gave 0.5688 gram tungsten trioxide, or 0.4511 gram tungsten, or 94.02 per cent. tungsten.

*Experiment 2.*—0.2239 gram greenish-blue substance gave 0.2644 gram tungsten trioxide, or 0.2096 gram tungsten, or 93.61 per cent. tungsten. From this the formula  $\text{W}_2\text{O}_5$  is deduced, containing theoretically 93.87 per cent. tungsten.

In group VI of the elements we do not find another similar oxide, with the exception of that of uranium,  $\text{U}_2\text{O}_5$ , prepared by Peligot, by treating a solution of  $\text{U}_2\text{Cl}_7$  with ammonia. It is a light green-colored, rather unstable compound.

The quantity of oxygen in  $\text{W}_2\text{O}_5$  was determined by reducing it in a current of hydrogen, as in a former experiment.

*Experiment.*—0.5321 gram greenish-blue substance gave 0.0358 gram water, or 0.0318 gram water, or 5.97 per cent. oxy-

gen, corresponding to the theoretical requirement of the formula, 6.13 per cent. oxygen.

$W_2O_3$  is decomposed by ammonia into metallic tungsten and tungstic acid; it precipitates silver from a solution of silver nitrate, insoluble in acids. The sulphuric acid solution, from the treatment of metallic tungsten with concentrated sulphuric acid, has the same properties as that obtained at a low temperature.

### III.

#### ACTION OF SULPHURIC ACID UPON METALLIC TUNGSTEN IN SEALED TUBES.

Sulphuric acid being so easily reduced by metallic tungsten at the ordinary atmospheric pressure, it was necessary to see what results would be obtained by allowing these two substances to act upon each other in sealed tubes and at different temperatures.

One gram of pure metallic tungsten and forty cc. of concentrated sulphuric acid were heated in a sealed tube for five hours at  $105^{\circ}C$ . At this temperature almost no reaction took place, so I increased the temperature to  $150^{\circ}C$ . for seven hours.

The contents of the tube had an entirely different appearance; there was a beautiful, clear, dark blue liquid, and a solid body of the same color, strongly adhering to the sides of the tube. Opening the tube, a very large quantity of sulphurous acid escaped with great violence.

The blue substance was well washed with alcohol and then ether, and dried at  $100^{\circ}C$ ., in an atmosphere of carbon dioxide. It is a homogeneous, dark blue mass, that precipitates metallic silver in brilliant scales, from a solution of silver nitrate; ammonia and alkalis decompose it into metallic tungsten and a soluble tungstate; the metallic tungsten proved to be very pure.

0.2115 gram gray substance gave 0.2667 gram tungsten trioxide, or 0.2115 gram tungsten, or 100 per cent. tungsten.

On adding water to the blue sulphuric acid solution, a green precipitate is formed, which in time becomes yellow from the oxidation to tungstic acid.

The blue substance, when ignited, is immediately transformed into yellow tungsten trioxide, from which the percentage of tungsten was calculated :

*Experiment 1.*—0.2512 gram blue substance gave 0.2802 gram tungsten trioxide, or 0.2221 gram tungsten, or 88.41 per cent. tungsten.

*Experiment 2.*—0.2136 gram blue substance gave 0.2493 gram tungsten trioxide, or 0.1977 gram tungsten, or 88.41 per cent. tungsten.

*Experiment 3.*—0.2555 gram blue substance gave 0.2848 gram tungsten trioxide, or 0.2258 gram tungsten, or 88.38 per cent. tungsten.

These three analyses were made with the product of three different tubes and correspond very well with the requirements of the formula of the tungsten sesquioxide :



containing theoretically 88.46 per cent. tungsten.

The quantity of oxygen was also determined by reduction in a current of hydrogen. The metallic tungsten remaining in the boat also corresponds to the formula of the sesquioxide.

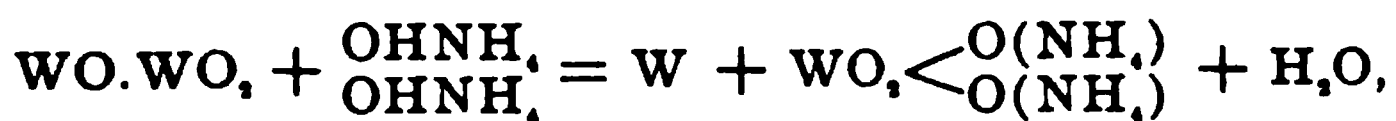
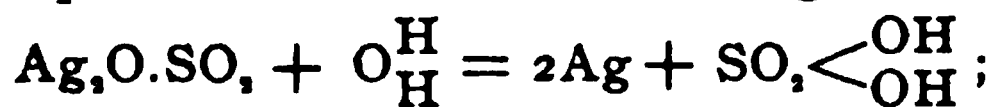
0.4111 gram blue substance gave 0.0530 gram water, or 0.0473 gram oxygen, or 41.52 per cent. oxygen.

0.3577 gram tungsten equals 88.44 per cent. tungsten.

This oxide has a great similarity to the sulphur sesquioxide ( $S_2O_3$ ), which element belongs to the same group of the periodic system as tungsten. The sesquioxide of sulphur is decomposed by water into sulphur, sulphurous acid, and sulphuric anhydride ( $SO_2$ ) and dissolves with a blue color in concentrated sulphuric acid. The difference between tungsten sesquioxide and sulphur sesquioxide is that the former is decomposed by ammonia, instead of by water, into metallic tungsten and tungsten trioxide ; probably tungsten dioxide is also formed but, being very unstable, it oxidizes very rapidly to tungsten trioxide.

The analogy between tungsten and sulphur is further shown by the property of silver sulphite to be decomposed by water into metallic silver and sulphuric acid.

The two equations demonstrate the analogy:



so we can consider  $W_2O_3$  to be the tungstite of tungsten.

Molybdenum sesquioxide differs from that of tungsten, by not being decomposed by ammonia or the alkalies. Chromium sesquioxide ( $\text{Cr}_2\text{O}_3$ ) differs by not being reduced by hydrogen, is not affected by heat, and is insoluble in acids.

To investigate the influence of heat in the reaction of sulphuric acid upon metallic tungsten, in sealed tubes, one gram of metallic tungsten was introduced into several tubes with varying quantities of concentrated sulphuric acid, and heated between  $170^\circ$  and  $180^\circ$  C., for seven hours. The tubes contained a blue liquid and a homogeneous blue substance. Upon opening them, sulphurous acid escaped. The blue substance was washed with alcohol and ether and then dried at  $100^\circ$  C. in an atmosphere of carbon dioxide.

This blue substance is of a lighter shade than the sesquioxide, is soluble in concentrated sulphuric acid, precipitates metallic silver from a solution of silver nitrate, and is decomposed by ammonia into metallic tungsten and tungstic acid.

Addition of water to the blue, sulphuric acid solution will precipitate a greenish-blue body, which becomes yellow ( $\text{WO}_3$ ) when it stands for some time. A certain quantity of this blue solution which had stood for three weeks in a small flask not well corked, changed its blue color to dark green, remaining perfectly clear. The sulphurous acid which it contained was driven off by passing a current of carbon dioxide until it was perfectly odorless; five cc. were then added to 190 cc. of standard potassium permanganate so as to find the state of oxidation of the tungsten. The quantity of tungsten was determined by precipitating the tungstic acid in ten cc. of the green solution, by addition of water. From different experiments the writer concluded that the green substance in solution must be  $\text{W}_2\text{O}_7$ .

Muthmann<sup>1</sup> has obtained the same oxide of molybdenum ( $\text{Mo}_2\text{O}_7$ ), by treating, in a flask, metallic molybdenum with concentrated sulphuric acid, at a low temperature.

This experiment was repeated several times between  $170^\circ$  and  $180^\circ$  C., always obtaining the same blue compound:

*Experiment 1.*—0.3651 gram blue substance gave 0.3992 gram tungsten trioxide, or 0.3166 gram tungsten, or 86.71 per cent. tungsten.

<sup>1</sup> *Loc. cit.*

*Experiment 2.*—0.2644 gram blue substance gave 0.2881 gram tungsten trioxide, or 0.2285 gram tungsten, or 86.43 per cent. tungsten.

*Experiment 3.*—0.3272 gram blue substance gave 0.3575 gram tungsten trioxide, or 0.2835 gram tungsten, or 86.70 per cent. tungsten.

*Experiment 4.*—0.2837 gram blue substance gave 0.3096 gram tungsten trioxide, or 0.2455 gram tungsten, or 86.53 per cent. tungsten.

From these results is deduced the following formula :



containing theoretically 86.47 per cent. tungsten.

Oxygen was determined by reducing the blue substance in a current of hydrogen gas, as in former experiments.

0.4561 gram blue substance gave 0.0690 gram water, or 0.0614 gram oxygen, or 13.46 per cent. oxygen, corresponding well to the formula  $\text{W}_2\text{O}_7$  with 13.53 per cent. oxygen.

A third series of experiments in sealed tubes was made at temperatures varying from 200°–250° C.

These results were not satisfactory, no homogeneous compounds, but mixtures of various colors, being obtained.

In tubes heated at 250° C. it was possible to see some yellow tungstic acid and, contrary to all former experiments, the sulphuric acid was perfectly colorless; probably higher oxides were formed, which are insoluble in sulphuric acid, whereas the lower oxides are soluble.

These traces of tungstic acid led to the hope that by increasing the temperature and heating for a long time, the metallic tungsten could be completely oxidized to tungstic acid; but all attempts were fruitless, probably on account of not being able to obtain a temperature sufficiently high.

#### IV.

##### ACTION OF SULPHUROUS ACID UPON METALLIC TUNGSTEN.

In one of the former experiments, where metallic tungsten was treated with concentrated sulphuric acid in an open flask at the ordinary atmospheric pressure, a few grains of the metal adhered to the neck of the flask far above the sulphuric acid.

When the reaction began by evolving sulphurous acid,

those grains of metallic tungsten slowly changed their color, becoming first green and then blue. As the temperature was low the tungsten could not have been oxidized by the oxygen from the air, as in ignition, and, as the reaction in the flask took place very gently, no sulphuric acid was thrown on the grains, so that the only explanation for this oxidation is that the sulphurous acid was readily reduced by tungsten.

This observation suggested the examination of the action of sulphurous acid upon tungsten under different conditions.

A small quantity of metallic tungsten was spread out in a hard glass tube, so as to offer a large surface for the action of the sulphur dioxide prepared by reducing sulphuric acid with copper. When all the air from the apparatus was driven out I began to heat the tungsten gently, but no reaction took place. Heating stronger to dull red, the gray color of the metal slowly began to become blue. When the whole mass appeared to be homogeneous, heating was discontinued, and the mass allowed to cool in the current of sulphur dioxide. Examining this blue substance carefully under the microscope a brown body seemed to be mixed with it, which was probably tungsten dioxide.

This experiment was repeated at various temperatures and for varying periods of time, but always more or less brown substance was formed. To prevent some parts of the metal being heated more than others, the tube was slowly turned, constantly exposing in this way new parts of the tungsten to the action of heat and of the sulphurous acid.

Obtaining no satisfactory results, the action of sulphurous acid upon metallic tungsten in sealed tubes was tried.

I first prepared a concentrated solution of sulphurous acid. The gas, after passing through three wash-bottles, entered a flask filled with distilled water, imbedded in a mixture of ice and salt; after complete saturation the contents of the flask, of a gelatinous consistency, was poured into a tube sealed at one end, containing metallic tungsten. During the sealing of the open end of the tube the sealed end was kept in the refrigerating mixture, so as not to lose any gas.

After the tube acquired the temperature of the surrounding air it was heated at  $110^{\circ}$  C. for ten hours. A green body was formed and a large quantity of free sulphur floated in the liquid.



Another tube was heated at 90° C. for the same length of time, when its contents had exactly the same appearance as that of the first tube.

On opening the tubes, the sulphurous acid escaped with great violence. Separation of the green substance from the free sulphur was tried by different mechanical means, amorphous sulphur being insoluble in carbon bisulphide; being unsuccessful in my attempts, I treated the green substance with carbon disulphide in a sealed tube for about half an hour, at 100° C. This operation succeeded very well, all the sulphur being dissolved. The green substance did not change in appearance; it was washed with water, alcohol, and ether, and dried in an atmosphere of carbon dioxide. The tungsten was determined by ignition.

*Experiment 1.*—0.2625 gram green substance gave 0.2649 gram tungsten trioxide, or 0.2100 gram tungsten, or 80.09 per cent. tungsten.

*Experiment 2.*—0.5012 gram green substance gave 0.5065 gram tungsten trioxide, or 0.4017 gram tungsten, or 80.14 per cent. tungsten.

*Experiment 3.*—0.3267 gram green substance gave 0.3305 gram tungsten trioxide, or 0.2621 gram tungsten, or 80.22 per cent. tungsten.

From these results is calculated the following formula :



containing theoretically 80.44 per cent. tungsten.

Knowing now that sulphurous acid will oxidize metallic tungsten, it was interesting to examine how far it would reduce tungstic acid.

The sealed tubes were prepared in exactly the same way as in the former experiments, taking tungstic acid instead of metallic tungsten. At 100° and 125° C. no change took place. At 150° C. the tungsten trioxide began to take a green color and free sulphur was liberated. The liquid was colorless and clear. I repeated this experiment at different temperatures, but did not succeed in obtaining a homogeneous compound.

Two of these tubes were lying on my desk for several months, exposed to the light and the direct rays of the sun. It was observed that the green substance darkened until it had a very dark green color, which apparently did not change any more and was homo-

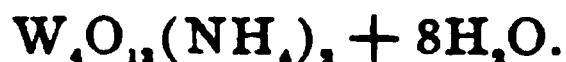
geneous. One end of the tube was opened, sulphurous acid escaped, and the green substance was rapidly washed with water, but it changed its dark green color to light green again. The free sulphur was separated by dissolving it in carbon disulphide, in a sealed tube; the result was a still lighter green substance, not homogeneous.

These experiments show that tungstic acid is reduced by sulphurous acid, but the resulting lower oxides are not stable. The action of light in this case is very interesting and might be the starting point of some important investigations.

The second tube was kept sealed over one year longer. During this time the dark green color of the substance gradually changed to light green, and on opening the tube no trace of sulphurous acid was perceptible, but instead a very strong odor of hydrogen sulphide. The liquid had a yellow color.

## V.

### ACTION OF HEAT UPON AMMONIUM METATUNGSTATE.



Berlin,<sup>1</sup> obtained an oxide of molybdenum, which, according to his analyses, has the formula  $\text{Mo}_2\text{O}_7 = 2\text{MoO}_3 \cdot \text{MoO}_3$ , a molybdate of molybdenum. He prepared it by heating strongly over a blast lamp, in a platinum crucible, a mixture of two parts of molybdenum trioxide and one part of ammonium molybdate. After cooling, the sides of the crucible were found to be covered with beautiful purple crystals, soluble in ammonia.

Later Muthmann<sup>2</sup> found that this oxide contained a considerable amount of nitrogen, which naturally lowered the percentage of molybdenum in it. He freed it of nitrogen by repeated boiling with hydrochloric acid and determined its formula to be



On account of the great analogy between tungsten and molybdenum, the same experiment was tried with ammonium metatungstate (one part) and tungstic acid (two parts), heated strongly for one hour over the blast lamp in a covered platinum crucible. The result was a mixture of blue and green oxides and undecomposed tungsten trioxide.

<sup>1</sup> *J. prakt. Chem.*, 49, 447.

<sup>2</sup> *Loc. cit.*

This mode of operating is very unsatisfactory, it being impossible to keep the air away from the contents of the crucible. The same mixture was introduced into a well-covered porcelain crucible and then into a large Battersea crucible, completely imbedded in powdered charcoal, the whole closed with refractory clay; in this way no air could possibly reach the hot contents of the crucible. It was heated for ten hours to white heat, in a wind furnace, and allowed to cool slowly over night. Opening the small crucible the sides were found covered with a beautiful crystalline substance of all possible colors.

Evidently, a reduction took place, but probably an inadequate quantity of the reducing agent was present to complete the reduction. As in this case, the hydrogen of ammonium metatungstate is the reducing agent, the experiment was repeated, taking the metatungstate alone and heating it for ten hours to a white heat.

The porcelain lid was fused to the crucible so that it had to be broken to reach its contents, which consisted of a perfectly homogeneous, gray, crystalline metallic substance, with a yellow reflex like brass filings, according to the exposure to the light. These crystals were carefully collected, a weighed quantity ignited and, from the tungstic acid obtained, it was concluded that it was metallic tungsten.

*Experiment 1.*—0.2429 gram gray crystals gave 0.3068 gram tungsten trioxide, or 0.2426 gram tungsten, or 99.87 per cent. tungsten.

*Experiment 2.*—0.1138 gram gray crystals gave 0.1434 gram tungsten trioxide, or 0.1137 gram tungsten, or 99.91 per cent. tungsten.

The temperature has a great influence in all these experiments upon the final result. Another experiment was performed by heating ammonium metatungstate for one and a half hours, only to bright red instead of to a white heat. The crucibles were prepared as in the foregoing experiments.

The small crucible, after the operation, contained a beautiful purple substance, with a yellow metallic reflex, insoluble in water, acids, and alkalies. It precipitated metallic silver from an ammoniacal solution of silver nitrate and easily burned to tungsten trioxide.

*Experiment 1.*—0.4075 gram purple substance gave 0.4181 gram tungsten trioxide, or 0.3315 gram tungsten, or 81.35 per cent. tungsten.

*Experiment 2.*—0.3112 gram purple substance gave 0.3183 gram tungsten trioxide, or 0.2524 gram tungsten, or 81.09 per cent. tungsten.

*Experiment 3.*—0.3626 gram purple substance gave 0.3713 gram tungsten trioxide, or 0.2945 gram tungsten, or 81.21 per cent. tungsten.

*Experiment 4.*—0.3874 gram purple substance gave 0.0819 gram water, or 0.0727 gram oxygen, or 18.78 per cent. oxygen. 0.3146 gram tungsten, or 81.20 per cent. tungsten.

From this was calculated the formula,



which would be the tungstate of the tungsten dioxide containing theoretically 81.17 per cent. tungsten and 18.83 per cent. oxygen.

In Roscoe and Schorlemmer's treatise, Vol. 2, p. 208, mention is made of a blue oxide, to which the formula  $W_2O_6$  is given. It was obtained by reducing tungstic acid in a current of hydrogen at 250° C. No properties of the oxide are given.

As small quantities of nitrogen could be occluded by the purple substance or even chemically combined, a small quantity of it was ignited in a current of hydrogen and the escaping gas conducted into a dilute cochineal solution. After one hour of this treatment the reduction was complete, but the cochineal solution had not changed in the least, demonstrating the complete absence of nitrogen.

Cochineal is a very delicate test for ammonia, the least trace changing its color to purple.

The substance remaining in the boat corresponds well with the requirements of the formula  $W_2O_6$  (81.17 per cent. tungsten).

0.3462 gram purple substance gave 0.2813 gram tungsten, or 81.25 per cent. tungsten.

## VI.

### ACTION OF ETHYLENE UPON TUNGSTIC ACID.

The well known property of ethylene of decomposing by heat into acetylene and methane, which in turn is decomposed

into acetylene and hydrogen, afforded a new method of reducing tungstic acid by nascent hydrogen, and not by the wet way, which necessarily must lead to new results.

A small quantity of tungsten trioxide was spread out in a hard glass tube and a rapid current of ethylene ( $C_2H_4$ ) passed through to expel all the air from the apparatus.

The ethylene gas was prepared by introducing drop by drop from a separating funnel a mixture of one part of alcohol and two parts of sulphuric acid into a flask containing twenty-five grams of absolute alcohol and 550 grams of sulphuric acid, heating very gently on a sand-bath. Ethylene gas prepared in this way always contains sulphurous acid and carbon dioxide; to free it from these admixtures it was conducted through three wash-bottles containing a concentrated solution of caustic potash, then through two towers, one filled with pieces of caustic potash, the other with calcined calcium chloride. The gas thus purified and dried, entered the tube containing the strongly heated tungstic acid. From time to time, the tube was turned, so as to offer fresh surfaces to the action of the heat and ethylene gas.

Soon the yellow color of the trioxide began to change and in a short time the whole quantity was transformed into a dark blue, homogeneous substance, retaining the crystalline form of the trioxide used. In the cold part of the tube minute drops of water were condensed.

After cooling in the current of ethylene, a weighed quantity of the blue substance was ignited in an open porcelain crucible. It oxidized very rapidly to yellow tungstic acid, but great was my astonishment, when weighing, to find that the weight of the tungstic acid *did not differ from that of the blue substance before the ignition.*

*Experiment 1.*—0.4037 gram blue substance gave 0.4037 gram tungsten trioxide.

*Experiment 2.*—0.4462 gram blue substance gave 0.4461 gram tungsten trioxide.

*Experiment 3.*—0.1152 gram blue substance gave 0.1150 gram tungsten trioxide.

*Experiment 4.*—0.1150 gram blue substance gave 0.1150 gram tungsten trioxide.

The presence of carbon being possible in this substance, a

combustion was made as with an organic substance. After heating strongly for five hours, the U-tube and potash bulbs were weighed, but there was no appreciable change of weight, showing complete absence of carbon and hydrogen.

Only in two ways can the writer explain this phenomenon. Either the substance is a new modification of tungstic acid, which is not probable on account of the formation of traces of water when treating tungstic acid with ethylene, or it is an oxide coming very near the limit of tungstic acid, and its molecular weight being so high that the small increase of weight when igniting it to tungstic acid cannot be determined.

The blue substance is insoluble in acids and alkalies, and does not precipitate silver from a solution of silver nitrate.

The action of acetylene ( $C_2H_2$ ) upon tungstic acid at different temperature was also tried, but in no case could any change be found in the appearance of the trioxide.

Only a very small deposit of carbon could be seen, due to the decomposition of acetylene by the heat.

## VII.

### ACTION OF THE OXIDES OF CARBON UPON TUNGSTIC ACID.

Muthmann<sup>1</sup> studied the action of carbon monoxide upon molybdic acid and succeeded in reducing it to metallic molybdenum.

The same reduction was tried with the tungstic acid, heating it strongly in a current of carbon monoxide, prepared by treating oxalic acid with sulphuric acid, conducting the escaping gas through two wash-bottles containing a strong solution of caustic potash, to retain any carbon dioxide, and then through two towers filled with calcium chloride. After five hours of intense heating in the boat, three distinct, differently colored layers were found; at the bottom the substance was brown, the second layer was blue, and the top layer was almost unaffected tungstic acid. The same portion was heated for five hours more, the brown substance increasing in quantity. It was then heated for over twenty hours, but no homogeneous substance could be obtained.

This shows the great affinity of tungsten for oxygen. Muthmann obtained metallic molybdenum after ten hours of the same

<sup>1</sup> *Loc. cit.*

treatment, whereas tungsten after thirty hours was still in the form of oxides.

When  $U_3O_8$  is heated for a long time in a current of carbon dioxide it is decomposed to  $U_2O_5$ .

Tungsten trioxide was subjected to the same treatment, heating a weighed quantity in a platinum crucible and introducing into it a current of dry carbon dioxide. Two hours of heating over the blast-lamp produced no change.

### VIII.

#### ACTION OF ALKALI METALS AND HALOID SALTS UPON TUNGSTIC ACID.

*A. Action of Potassium Bromide.*—It was found that if tungstic acid is heated with a solution of potassium bromide and a few drops of hydrochloric acid, a reaction takes place. The solution takes on a green color which, upon continued heating, again becomes yellow. This reduction led to the idea that by fusing a mixture of potassium bromide and tungstic acid, well-defined bodies could be obtained.

Three grams of tungstic acid and ten grams of potassium bromide, thoroughly mixed, were introduced into a well-covered porcelain crucible and then imbedded in powdered charcoal in a larger crucible, as in former experiments, and the whole heated to white heat for six hours in a wind furnace. After thorough cooling the small crucible was opened and a gray, crystalline metallic powder was found. After washing it with water and drying at  $110^\circ\text{C}$ ., a weighed quantity was ignited; it burned rapidly to yellow tungstic acid.

*Experiment 1.*—0.0987 gram gray substance gave 0.1238 gram tungsten trioxide, or 0.0982 gram tungsten, or 99.5 per cent. tungsten.

*Experiment 2.*—0.3384 gram gray substance, gave 0.4266 gram tungsten trioxide, or 0.3383 gram tungsten, or 99.97 per cent. tungsten.

This gray substance is consequently metallic tungsten.

The same mixture was treated at different temperatures and for varying periods, but no well-defined bodies were obtained; probably by varying the proportions of the two substances, other well-defined compounds would result.

*B. Action of Potassium Iodide.*—Schulze<sup>1</sup> fused potassium iodide and tungstic acid, but does not seem to have obtained any well-defined bodies, as he does not give any analytical results.

Two grams of potassium iodide and one gram of tungstic acid were treated as in the experiments under *A*.

The small crucible contained a beautiful purple, crystalline substance, precipitating metallic silver from an ammoniacal solution of silver nitrate, insoluble in acids and alkalies. This substance has all the characteristics of that obtained from the action of heat upon metatungstate of ammonium. The amount of tungsten calculated from the tungstic acid obtained by ignition of a weighed quantity of the purple substance, corresponds well with the requirements of the formula  $W_2O_5$ , with 81.17 per cent. tungsten.

*Experiment 1.*—0.2131 gram purple substance gave 0.2181 gram tungsten trioxide, or 0.1729 gram tungsten, or 81.14 per cent. tungsten.

*Experiment 2.*—0.3127 gram purple substance gave 0.3202 gram tungsten trioxide, or 0.2539 gram tungsten, or 81.19 per cent. tungsten.

Another mixture of one gram tungstic acid and four grams potassium iodide, after the same treatment as above, gave quite a different result. Metallic tungsten was obtained.

0.1225 gram gray powder gave 0.1544 gram tungsten trioxide, or 0.1224 gram tungsten, or 99.98 per cent. tungsten.

*C. Action of Potassium Chloride.*—One gram tungstic acid and two grams potassium chloride, were treated as under *B*, for five hours. The sides of the crucible were covered with beautiful, glittering, gray crystals, which were metallic tungsten.

0.1066 gram gray powder gave 0.1340 gram tungsten trioxide, or 0.1065 gram tungsten, or 99.90 per cent. tungsten.

The action of the haloid salts of the other alkali metals was also studied, and it was found that the reducing power diminishes with the lower atomic weight; the temperature must be higher and the action of heat longer.

*D. Action of Metallic Potassium.*—The remarkable reducing action of the haloid salts of the alkali metals cannot be explained otherwise than that at a very high temperature they are dissocia-

<sup>1</sup>*J. prakt. Chem.*, 21, 439.



ted into their component parts. The alkali metal being, so to say, in the nascent state, combines with eagerness with the oxygen of the tungstic acid and sets free metallic tungsten.

The bottom of a porcelain boat was covered with small, bright pieces of metallic potassium, and on top of it tungstic acid. The whole was introduced into a hard, glass tube, through which a current of dry nitrogen passed; the nitrogen was prepared by dropping a concentrated solution of sodium nitrite into a hot, concentrated solution of ammonium chloride, the gas passing through two calcium chloride towers, before entering the tube. After all the air was expelled from the apparatus, the tube was gently heated under the boat, increasing the temperature slowly, until the potassium began to melt. Soon white vapors began to rise from the boat, condensing to a white powder in the cooler parts of the tube. Increasing the temperature a little, blue and purple fumes of the different oxides of potassium were formed. The reduction began to be violent, when suddenly a deflagration took place, and all action ceased immediately.

The boat was allowed to cool in the atmosphere of nitrogen. It contained a gray, spongy mass, fused to the side of the boat and covered with a white coating ( $K_2O$ ). After washing with water, a gray metallic, very finely divided powder was left, which was metallic tungsten.

0.1892 gram gray powder gave 0.2385 gram tungsten trioxide, or 0.1891 gram tungsten, or 99.91 per cent. tungsten.

If, instead of washing the contents of the boat with water, hydrochloric acid is used, a clear, dark blue solution is obtained, which oxidizes very rapidly to a green-colored liquid and then a yellow-greenish precipitate is formed, which in time becomes entirely yellow. The supernatant liquid is colorless and clear. The undissolved residue in the boat is gray metallic tungsten.

0.1965 gram gray powder gave 0.2477 gram tungsten trioxide, or 0.1964 gram tungsten, or 99.95 per cent. tungsten.

*E. Action of Metallic Sodium*—The previous experiment was repeated, but instead of potassium, metallic sodium was used.

The reaction takes place at a higher temperature, is not so violent, and the deflagration liberates less heat. The contents of the boat were much darker in color after being washed. The substance is almost black and flocculent, burning rapidly to

tungstic acid when ignited. It proved to be metallic tungsten.

0.1190 gram black substance gave 0.1500 gram tungsten trioxide, or 0.1189 gram tungsten, or 99.91 per cent. tungsten.

## IX.

### ACTION OF METALLIC MAGNESIUM UPON TUNGSTIC ACID.

As magnesium is a much less active element than the alkali metals, the writer thought that perhaps it would enable him to obtain new oxides.

In a porcelain boat was placed a mixture of one gram tungstic acid and 0.75 gram metallic magnesium powder, the whole introduced into a hard glass tube and a current of dry nitrogen passed over it. The tube was gently heated under the boat until it was dull red in color, when a violent deflagration took place, generating so much heat that the tube became quite red, and broke in several places.

After cooling in the atmosphere of nitrogen the boat was taken out; it contained a very hard, gray substance, firmly adhering to the sides of the boat. It was covered with magnesium oxide and emitted a peculiar, garlic-like odor. After detaching this gray mass from the sides of the boat, it was ground in a mortar to a fine powder. On adding a little water, it began to effervesce strongly. The escaping gas was collected in a test-tube, and in bringing it to a flame, a little puff was heard, showing the decomposition of water.

Neither magnesium nor tungsten decompose water at the ordinary temperature. Then this powder must be an alloy of the two metals.

A certain quantity of the gray substance was left on the sides of the boat, to which was added a drop of hydrochloric acid; a little explosion occurred, with a blue flame. This explosion is due to a magnesium silicide, formed by heating magnesium strongly in contact with the silicon of the porcelain boat,



which is easily decomposed by hydrochloric acid, the free silicon forming with hydrogen, siliconhydride,  $\text{SiH}_4$ , an inflammable gas at the ordinary temperature.

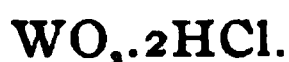
This experiment of the reduction of the tungstic acid with magnesium in an *iron* boat was repeated, to prevent the formation of the

magnesium silicide. The result was a gray mass as before, decomposing water and generating hydrogen when treated with hydrochloric acid; the residue is then insoluble in acids, except in aqua regia, and is an alloy of magnesium and tungsten.

Filtering off the hydrochloric acid from the gray mass, the drops toward the end of the funnel were seen to take on a dark blue color, which during the fall to the bottom of the flask changed to yellow without forming any precipitate. If water is added to this filtrate yellow tungstic acid is precipitated.

A portion of the gray mass was treated with hydrochloric acid in an atmosphere of carbon dioxide, filtered in the same gas into a flask also filled with it. In this case the hydrochloric acid solution did not take first a blue color, but it immediately became yellow, and water did not precipitate tungstic acid in the cold, but only upon heating.

To determine the state of oxidation of the tungsten in this solution, ten cc. were added to 190 cc. of potassium bichromate solution (tenth-normal), but its standard did not change, showing that the tungsten is at its highest state of oxidation and must form like molybdenum, an oxychloride of tungsten,



This oxychloride of tungsten is probably analogous to chlorochromic acid,  $\text{CrO}_3 \cdot \text{HCl} = \text{CrO}_3 \cdot \text{HCl}$ , and to chlorosulphonic acid,  $\text{SO}_3 \cdot \text{HCl} = \text{SO}_3 \cdot \text{HCl}$ , being decomposed when heated into anhydride.

The gray substance precipitates metallic silver from a solution of silver nitrate. As it dissolves with difficulty even in aqua regia, I fused it with potassium bisulphate, obtaining soluble magnesium sulphate and insoluble tungstic acid, which were separated by filtration. In the filtrate magnesium was precipitated as magnesium-ammonium phosphate.

0.4598 gram gray substance gave 0.4179 gram tungsten trioxide, or 0.3314 gram tungsten, or 72.08 per cent. tungsten.

0.5916 gram gave 0.1279 gram magnesium pyrophosphate or 27.81 per cent. magnesium.

Different experiments gave about the same results, with slight variations.

Instead of reducing the tungstic acid with magnesium in a current of nitrogen, carbon dioxide was used. The reduction took place very slowly, at a very high temperature, and without deflagration. The resulting product had the color of steel, decomposed in water, and apparently also absolute alcohol when hot.

## THE OXYNITRIDES OF TUNGSTEN.

### I.

#### ACTION OF AMMONIUM CHLORIDE UPON TUNGSTIC ACID.

Continuing the experiments of the reduction of tungstic acid by various reducing agents, a large number of bodies containing tungsten, nitrogen, and oxygen were the result.

No suboxides or true nitrides of tungsten could be obtained, the affinity of tungsten to oxygen being so great that it was impossible to substitute the last traces of oxygen by nitrogen.

A long series of experiments was made under varying conditions, and the conclusion was drawn that nitrides of tungsten can be obtained only by treating the chlorides of tungsten.

Ammonium chloride being easily dissociated by heat, a mixture was made of tungstic acid and ammonium chloride in excess and heated in a covered porcelain crucible over the blast lamp, until no more fumes were evolved. Opening the crucible, there was found on the top some slightly decomposed tungstic acid, underneath a mixture of blue and green oxides, and at the bottom a black crystalline substance. Some of the crystals reflected the light so strongly that they were first taken to be some small pieces of glass that had accidentally found their way into one of the reagents used.

This black substance was again twice treated with ammonium chloride, succeeding in this way in obtaining a homogeneous, black, very light substance, insoluble in acids and alkalies.

The sides of the crucible were covered with a black, metallic deposit, which suggested the presence of nitrogen on account of its similarity with nitrides of chromium and uranium.

To ascertain the presence or absence of nitrogen, the well washed and dried black substance was treated in a hard glass tube with hydrogen, the gas escaping from the tube being conducted into a cochineal solution, which changed its color very

soon to purple, thus, showing the formation of ammonia, and consequently the presence of nitrogen in the black substance. A nitride was obtained instead of a lower oxide. The nitrogen was estimated by Dumas' method.

It was also important to know whether this substance contained hydrogen. A weighed quantity was ignited in a current of oxygen, taking all precautions to prevent the formation of nitrogen oxides. Any water formed was absorbed in a U-tube, filled with freshly calcined calcium chloride. After five hours heating, the increase of weight of the U-tube was only 0.0002 gram, corresponding to 0.08 per cent. hydrogen, so that hydrogen is absent.

If the black substance is ignited in a current of hydrogen abundant water vapors are condensed in the cooler parts of the tube, showing the presence of oxygen.

The tungsten was estimated by igniting a weighed quantity of the black substance in an open crucible. Even prolonged and very strong heating will not oxidize it completely to yellow tungstic acid. In one experiment the substance was ignited for two days, taking every precaution to prevent the combustion gases from the burner entering the crucible; but pure yellow tungsten trioxide was not obtainable, a large quantity remaining black, some being dark and some light green. To complete the oxidation I had to use aqua regia repeatedly and obtained in this way an almost complete oxidation; the tungstic acid still had a greenish tint.

All the oxynitrides, obtained by different methods, are oxidized with difficulty, showing a great affinity between tungsten and nitrogen; even aqua regia breaks down this intimate union of the two elements only after long action.

*Experiment 1.*—0.2837 gram black substance gave 0.3188 gram tungsten trioxide, or 0.2528 gram tungsten, or 89.10 per cent. tungsten.

0.2047 gram black substance gave 0.0192 gram nitrogen, or 9.41 per cent. nitrogen.

0.4518 gram black substance gave 0.0077 gram water, or 0.0068 gram oxygen, or 1.51 per cent. oxygen.

From this is deduced the formula  $W_{10}N_2O_4$ .

	Calculated.	Found.
Tungsten .....	89.28	89.10
Nitrogen .....	9.16	9.41
Oxygen .....	1.55	1.51

*Experiment 2.*—0.1293 gram black substance gave 0.1366 gram tungsten trioxide, or 0.1083 gram tungsten, or 83.75 per cent. tungsten.

0.2718 gram black substance gave 0.03493 gram nitrogen, or 12.85 per cent. nitrogen.

0.5006 gram black substance gave 0.0182 gram water, or 0.0162 gram oxygen, or 3.23 per cent. oxygen.

From this the following formula is derived :  $W_3N_4O_4$ .

	Calculated.	Found.
Tungsten.....	83.63	83.75
Nitrogen .....	12.72	12.85
Oxygen.....	3.63	3.23

*Experiment 3.*—0.3247 gram black substance gave 0.3539 gram tungsten trioxide, or 0.2806 gram tungsten, or 86.44 per cent. tungsten.

0.3192 gram black substance gave 0.02432 gram nitrogen, or 7.61 per cent. nitrogen.

0.4758 gram black substance gave 0.0311 gram water, or 0.0276 gram oxygen, or 5.80 per cent. oxygen.

From this the following formula is calculated :  $W_3N_4O_4$ .

	Calculated.	Found.
Tungsten.....	86.14	86.44
Nitrogen .....	7.86	7.61
Oxygen .....	5.99	5.81

*Experiment 4.*—0.1997 gram black substance gave 0.2213 gram tungsten trioxide, or 0.1755 gram tungsten, or 87.88 per cent. tungsten.

0.3125 gram black substance gave 0.02176 gram nitrogen, or 6.96 per cent. nitrogen.

0.3894 gram black substance gave 0.0222 gram water, or 0.0198 gram oxygen, or 5.08 per cent. oxygen.

From this the following formula is derived :  $W_3N_4O_4$ .

	Calculated.	Found.
Tungsten .....	88.17	87.88
Nitrogen .....	6.71	6.96
Oxygen.....	5.11	5.08

Hoping to obtain better results by increasing the temperature, a mixture of ten grams tungstic acid and twenty grams of ammonium chloride was made in a well-covered, smooth crucible, the whole placed in a large crucible, then filled with powdered charcoal and closed with a lid and fire-clay, so that no air could possibly affect the reduction. It was heated in a wind furnace to bright redness for five hours. After thorough cooling, the small crucible was opened and several crystalline substances of different colors were found.

Different proportions of the mixture and different temperatures were tried, but a homogeneous substance could not be obtained. Finally a mixture was made of ten grams of tungstic acid and sixty grams ammonium chloride, heated to white heat for twelve hours and a black, amorphous powder obtained, insoluble in acids and alkalies, and attacked with difficulty by aqua regia.

0.3278 gram black powder gave 0.4099 gram tungsten trioxide, or 0.3250 gram tungsten, or 99.14 per cent. tungsten.

Consequently it is metallic tungsten. As it must contain some impurity, probably nitrogen, it was boiled for several hours with hydrochloric acid, frequently changing the acid; after washing it with water and drying at  $105^{\circ}\text{C.}$ , a weighed quantity was ignited; the hydrochloric acid had removed most of the impurities.

0.2867 gram black powder gave 0.3609 gram tungsten trioxide, or 0.2863 gram tungsten, or 99.85 per cent. tungsten.

After a great many experiments I came to the conclusion that it is impossible to obtain a nitride by means of ammonium chloride, and that it is also impossible to obtain at will and every time the same well-defined body, the result depending entirely upon the temperature, which cannot be regulated nor controlled in this case.

## II.

### ACTION OF POTASSIUM CYANIDE UPON TUNGSTIC ACID.

If tungstic acid is added to potassium cyanide in fusion it will be completely dissolved without changing the color of the fused cyanide. If we continue the addition of tungstic acid a point will be reached when it will no more be dissolved, but instead a black mass will be formed.

Tungsten trioxide will also be dissolved in an aqueous solution of potassium cyanide. If alcohol is added to this solution, and then ether, a heavy yellow, sometimes brown liquid will separate, which after a few weeks will deposit a black substance insoluble in acids or alkalies.

The black substance obtained by fusing tungstic acid and potassium cyanide, was well washed with water, a difficult operation. Being very light, it takes considerable time to settle, and even the densest filter paper will not retain it.

A qualitative test for nitrogen and oxygen proved the presence of both elements. As potassium cyanide contains carbon, the possibility of its presence in the black substance suggested itself; a combustion, as for organic compounds, showed complete absence of carbon.

A weighed quantity was ignited in an open porcelain crucible, for several hours, adding from time to time a few drops of aqua regia, but it was not possible to obtain a pure yellow tungstic acid, as it persistently retained a greenish color.

Nitrogen was determined as before according to Dumas' method.

0.3744 gram black substance gave 0.3913 gram tungsten trioxide, or 0.3103 gram tungsten, or 82.87 per cent. tungsten.

0.2040 gram black substance gave 0.02027 gram nitrogen, or 9.03 per cent. nitrogen.

0.4001 gram black substance gave 0.0324 gram water, or 0.0288 gram oxygen, or 7.21 per cent. oxygen.

From this the following formula is derived:  $W_3N_2O_8$ .

	Calculated.	Found.
Tungsten .....	82.82	82.86
Nitrogen .....	10.07	9.93
Oxygen .....	7.19	7.21

An interesting point remained to be determined: whether the reducing power of the potassium cyanide would increase with the temperature.

To this end a crucible containing ten grams of tungstic acid and fifteen grams potassium cyanide was imbedded in charcoal inside of a large crucible, as in former experiments, and heated to white heat for twelve hours, in a wind furnace. After thorough cooling the small crucible was twisted out of shape, showing that the temperature must have been very high; its



sides were incrustated with small, perfectly round, *bright, silver-white metallic globules*, very brittle, insoluble in acids, and attacked with difficulty even by aqua regia. An ignition showed that these globules were very pure metallic tungsten.

0.1752 gram crushed globules gave 0.2209 gram tungsten trioxide, or 0.1752 gram tungsten, or 99.97 per cent. tungsten.

In the literature of tungsten no mention is found of its preparation in this form.

The same mixture of ten grams tungsten trioxide and fifteen grams potassium cyanide was similarly treated as before, but instead of heating to white heat, it was heated to bright red. The result was a black oxynitride.

0.2431 gram black substance gave 0.2612 gram tungsten trioxide, or 0.2071 gram tungsten, or 85.21 per cent. tungsten.

0.3081 gram black substance gave 0.02295 gram nitrogen, or 7.45 per cent. nitrogen.

0.3724 gram black substance gave 0.0307 gram water, or 0.0272 gram oxygen, or 7.32 per cent. oxygen.

The following formula is derived :  $W_7N_8O_{11}$ .

	Calculated.	Found.
Tungsten .....	85.18	85.21
Nitrogen .....	7.40	7.45
Oxygen.....	7.40	7.32

A thorough mixture of ten grams tungstic acid, ten grams potassium cyanide, and ten grams finely powdered charcoal was treated under the same conditions as before, heating to bright red. A black powder was the result, mixed with the charcoal, which could not be separated, both substances having about the same density.

### III.

#### ACTION OF CYANOGEN UPON TUNGSTIC ACID.

As potassium cyanide reduces tungstic acid to metallic tungsten at a very high temperature, it was thought that cyanogen would have perhaps a greater reducing power, and that metallic tungsten could be obtained at a lower temperature.

A porcelain boat containing tungsten trioxide was introduced into a hard glass tube ; after driving out the air from the apparatus with dry cyanogen, prepared by dropping a concentrated solution of potassium cyanide into a hot concentrated solution of copper sulphate, the boat was gently heated. At a red heat

the trioxide began to change its color to brown, which soon became darker, and with the increase of temperature finally black. It is a very beautiful, glossy substance, like velvet, with a bluish tint. Like all the other oxynitrides it is oxidized with difficulty by ignition and aqua regia.

1.1140 gram black substance gave 1.1323 gram tungsten trioxide, or 0.0898 gram tungsten, or 80.61 per cent. tungsten.

0.3814 gram black substance gave 0.1473 gram nitrogen, or 3.86 per cent. nitrogen.

0.3227 gram black substance gave 0.0564 gram water, or 0.0502 gram oxygen, or 15.55 per cent. oxygen.

The following formula is derived:  $W_8N_3O_{11}$ .

	Calculated.	Found.
Tungsten.....	80.84	80.61
Nitrogen .....	3.69	3.86
Oxygen .....	15.46	15.55

This experiment was repeated several times, heating as long as twenty hours. The hard glass tube became soft, but no metallic tungsten could be obtained. The result was always an oxynitride.

#### SEPARATION OF MOLYBDENUM FROM TUNGSTEN.

When these two metals are together in the form of their trioxides they can be quantitatively separated by Debray's method.<sup>1</sup>

If molybdenum and tungsten are in solution they can be separated by Rose's method. To their solution tartaric acid is added and then a current of hydrogen sulphide is passed in, precipitating the molybdenum as sulphide ( $MoS_3$ ), while tungsten remains in solution.

Friedheim and Meyer<sup>2</sup> found that this method is not quite satisfactory, a certain quantity of molybdenum always escaping the action of the hydrogen sulphide and thus remaining in solution.

Tungstic acid is found to be entirely insoluble in concentrated or dilute sulphuric acid, hot or cold, whereas molybdenum trioxide is very easily and rapidly dissolved, so that we have in this department a very simple and exact method for the separation of the two elements.

UNIVERSITY OF PENNSYLVANIA.

<sup>1</sup> *Loc. cit.*

<sup>2</sup> *Ztschr. anorg. Chem.*, 1, 76.

# THE DISTRIBUTION OF THE PRECIOUS METALS AND IMPURITIES IN COPPER AND SUGGESTIONS FOR A RATIONAL MODE OF SAMPLING.

BY EDWARD KELLER.

Received January 8, 1897.

IN order to be able to conduct intelligently the sampling of copper, of various forms and grades, solid or in molten furnace charges, knowledge of this subject is essential. Yet figures and tests have been persistently withheld from publication, and the books at our command give us little or no information. This gap in our literature has led to a series of experiments, the results of which here follow :

Nearly all gold- and silver-bearing copper, destined for shipment, is cast into the form of bars or pigs. For the sampler the question arises: Does copper so cast remain homogeneous, or does it not? If so, no difficulty would occur; but experience teaches us that the cast metal is not homogeneous and this leads to the study of the behavior of the precious metals and impurities in copper, when the latter changes from the molten to the solid state.

For the purpose of the experiments, all available grades of copper were selected, and all of them subjected to the same conditions, which is important for the purpose of proper comparison.

The molten copper, directly obtained from reverberatory and blast furnaces, was cast in a cast iron mold, the sides and bottom of which were one inch thick, and would, therefore, give the copper a fair length of time to chill. The inside dimensions of the mold were: length, ten inches; width, nine inches; and depth five inches, which dimensions were the same for the blocks of copper obtained.

The accompanying figure (1) illustrates the method employed to obtain samples from these blocks. *A* was cut away, and the face thus produced on *B* was marked off over one-half of its surface into one inch squares (it being assumed that the other half would behave the same, or nearly so), and by drilling through the center of each square, three inches deep, the individual samples, as indicated by  $S_1, S_2, S_3, S_4, S_5$ , etc., obtained.

In this way each block should have yielded twenty-five samples. But with the unrefined copper, the uppermost inch of the

block consisted mostly of blisters and some slag, while with the refined material the surface, on setting, had sunken nearly one inch. With all but one block, therefore, twenty samples of each only were considered.

In Fig. 2 are given the silver and gold determinations of a

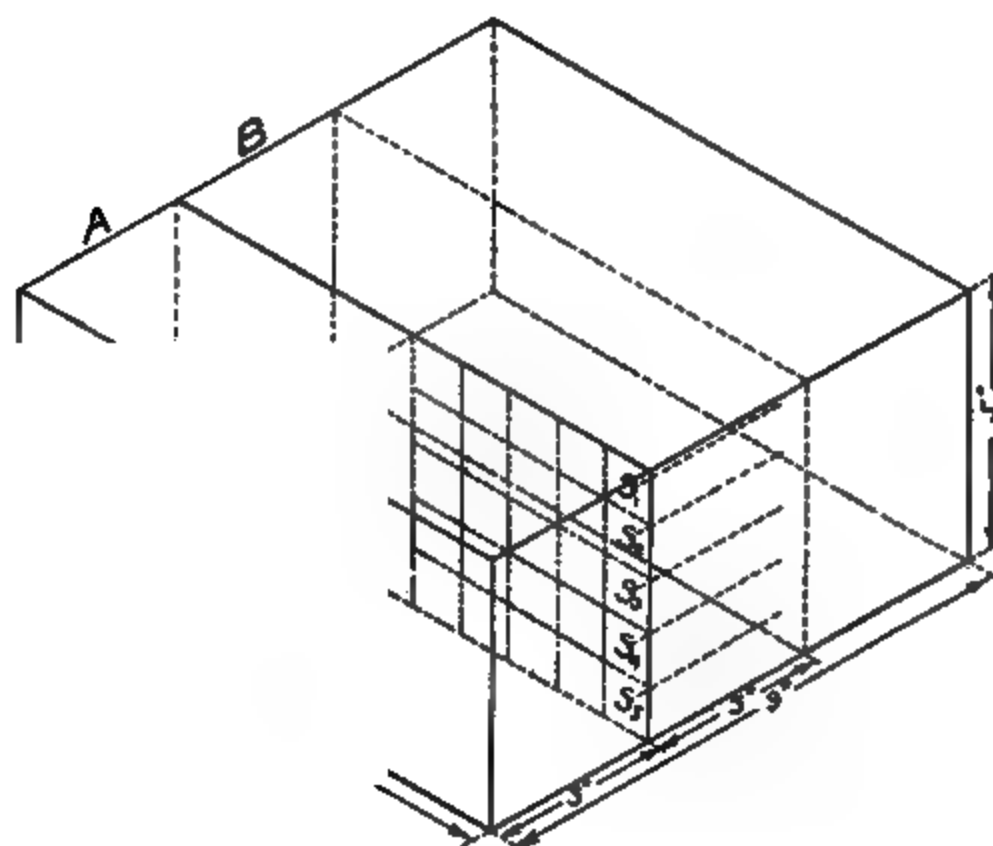


Fig. 1.

blister-copper for the twenty regular samples, as also of the uppermost crust, over the blisters. The amount of the precious

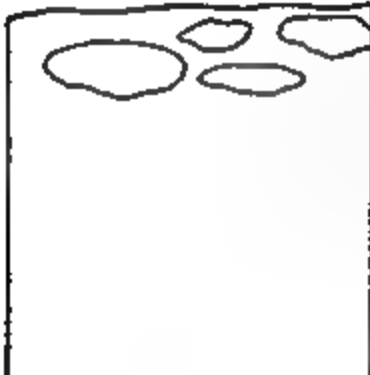
		132.3		116	
		1789	2011	116	1007
		.34	.34	.24	.22
		130.1	1352	194.5	122
		.32	.34	.34	.26
		104.5	117	122.3	105.1
		.22	.26	.30	.26
		713	703	69.8	69.8
		.24	.22	.22	.22

Fig. 2.

metals is expressed in ounces per ton, in this, as well as all the following samples.

For the purpose of a general analysis of this block, samples were taken from the bottom, center, and top of *B* (Fig. 1). They gave the following results :

	Bottom. Per cent.	Center. Per cent.	Top. Per cent.
Ag.....	0.248	0.641	0.454
Au.....	0.00068	0.00109	0.00089
Pb.....	0.002	0.058	0.019
Bi.....	0.005	0.055	0.024
Sb.....	0.048	0.157	0.099
As.....	0.034	0.108	0.074
Te.....	0.004	0.027	0.019
S.....	0.040	0.112	0.047
	<hr/> 0.382	<hr/> 1.159	<hr/> 0.737

A glance at these figures convinces us that in this case a concentration, or segregation, of precious metals and impurities has taken place in a high degree towards the center ; not the geometrical center but the center of solidification, which latter naturally lies above the former, more heat being given off at the bottom to the metallic mold than to the air on top, for which reason solidification proceeds more rapidly from the bottom.

Of the degree of concentration we best receive an idea by comparing each element of the bottom sample with the corresponding element of the center sample. Dividing the value for the latter by the value for the former, gives us the degree of concentration from bottom to center. We have accordingly :

Element.	Concentration.
Ag.....	2.59
Au.....	1.60
Pb.....	29.00
Bi.....	11.00
Sb.....	3.27
As.....	3.18
Te.....	6.75
S.....	2.80

The difference of behavior of the various elements is surprising.

That a sample, which is not a correct average from a bar, or pig, of such copper, might lead to great errors regarding its silver and gold contents, needs no further illustration. But also the copper determinations would be far from being correct should they be made of a sample from any one part of such bar

or pig. This will at once become evident if we take the copper by difference (100 — amount of impurities) in the three analyzed samples :

	Bottom. Per cent.	Center. Per cent.	Top. Per cent.
Copper by difference .....	99.618	98.841	99.263

Fig. 3 represents a block of refined converter-copper, with

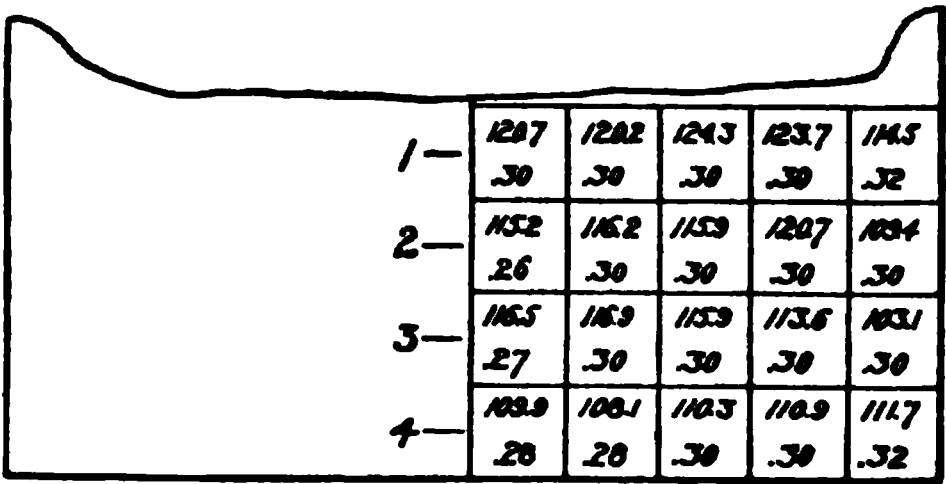


Fig. 3.—Block of Refined Converter-Copper with Determinations.

silver and gold as found in the respective samples.

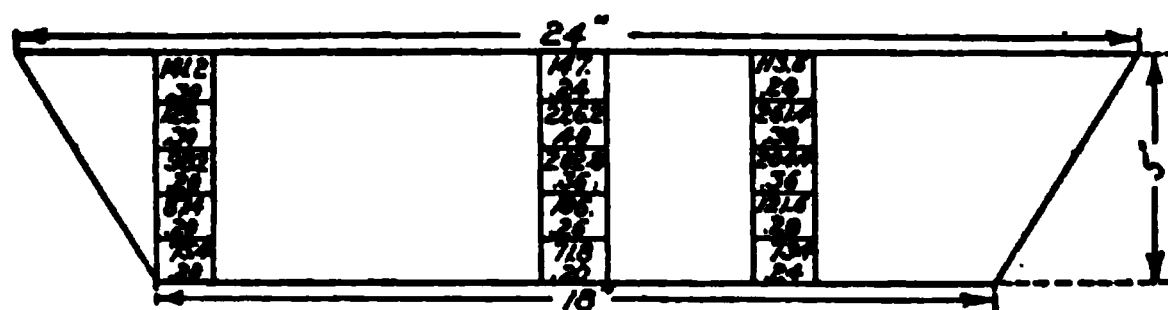
General analyses were made of Sample 1, Samples 2 and 3 combined, and Sample 4, with the following results :

	1. oz.	2 and 3.	4. oz.
Ag.....	120.7		109.9
Au.....	0.30		0.28
	Per cent.	Per cent.	Per cent.
Bi .....	0.0026	0.0017	0.0013
Sb .....	0.057	0.060	0.051
As .....	0.022	0.021	0.014
Te .....	0.008	....	0.0056
O .....	0.293	....	0.200
(Cu <sub>2</sub> O.....	2.687	....	1.800)

Among copper metallurgists it is customary to give the amount of cuprous oxide instead of the oxygen. Both figures are, therefore, here inserted.

It will be noticed that the concentration of the precious metals and impurities in this second sample is analogous to the first ; they have moved from the sides and bottom towards the center and top ; but the degree of concentration is very much reduced. This may easily be explained by the fact that the refined copper contains a much smaller amount of impurities than the blister copper, thereby giving it a higher melting-point and a higher conductivity for heat, both properties favoring a more rapid solidification, and consequently shortening the time for the molecules to move towards the center.

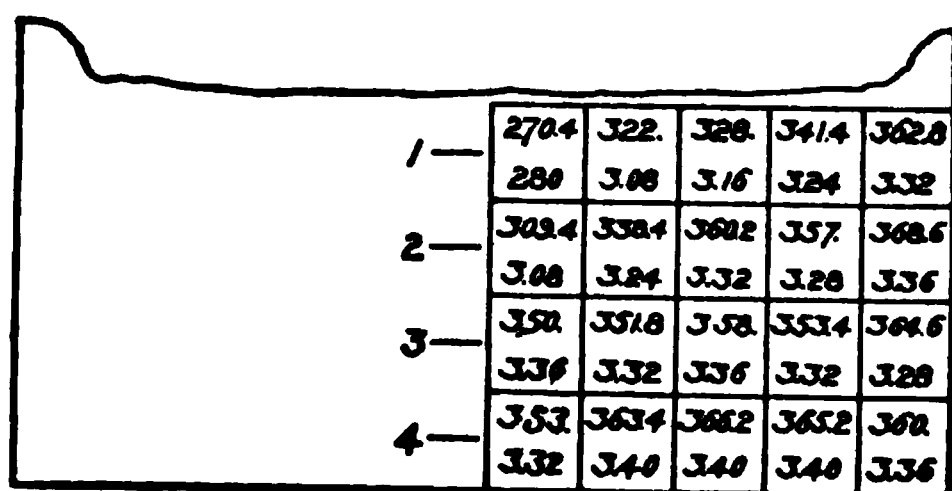
**Fig. 4** represents an original converter pig, from which



**Fig. 4.—Converter Pig Copper.**

kind of copper the previous sample was derived. The pig was drilled vertically, through the center. The values found for silver and gold show no variation, as to distribution, from the two other samples already illustrated.

**Fig. 5 represents a refined copper, in which the amounts of**



**Fig. 5.—Refined Copper.**

**silver and gold, as well as the impurities, are considerably higher than in those represented by Figs. 2 and 3.**

**Samples 1, 2, 3, and 4 were analyzed as follows :**

	1.	2.	3.	4.
	Ounces.	Ounces.	Ounces.	Ounces.
Ag .....	270.4	309.4	350.0	353.0
Au .....	2.80	3.08	3.36	3.32
	Per cent.	Per cent.	Per cent.	Per cent.
Pb .....	0.204	0.248	0.351	0.392
Sb .....	0.163	0.185	0.211	0.217
As .....	0.134	0.151	0.197	0.212
Te .....	0.0125	. .	0.015	0.0195

Here, again, we see differences in the quantities of the elements in each sample ; that is, concentration. But if we compare these with the former samples we observe the astonishing fact, that now we have the maxima in the position, where before were the maxima, and vice versa. In other words, we find a copper in which the conditions have been reversed. Instead of the precious metals and impurities concentrating towards the

center, it is now the copper which takes that place, and leaves the former concentrated towards the outside.

Fig. 6 represents a black copper from a blast furnace, but

1 —	379.0 1.04	387.6 1.00	378 1.00	427.2 .92	507.8 1.00
2 —	337.8 1.00	362.2 .92	384 .92	399.8 1.04	489.4 1.04
3 —	350.2 .88	355.8 .88	361 .92	392.6 1.04	474.6 1.04
4 —	364.4 1.00	374.4 1.00	381.2 1.00	402.8 1.08	480.8 1.04
5 —	425.6 1.04	424 1.04	432.8 1.04	458 1.00	505.6 1.00

Fig. 6.—Black Copper Showing all Characteristics of Blister Copper.

showing all the characteristics of a blister copper. It is, in its relations to our subject, an analogon to the preceding sample.

Five samples were subjected to general analysis :

	1. Ounces.	2. Ounces.	3. Ounces.	4. Ounces.	5. Ounces.
Ag ....	379.0	337.8	350.2	364.4	425.6
Au ....	1.04	1.00	0.88	1.00	1.04
	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
Pb.....	2.487	2.445	2.366	2.531	2.851
Bi.....	0.400	0.360	0.360	0.310	0.420
Sb.....	3.438	3.073	2.820	2.789	3.929
As.....	0.705	0.716	0.630	0.627	0.706
Te.....	0.892	0.768	0.814	0.856	0.882
S.....	0.538	0.467	0.462	0.487	0.469
Fe.....	4.220	5.050	4.430	5.460	3.500

Scrutinizing the values for the various elements, it will be seen that sulphur and iron have behaved differently from the rest. Sulphur shows irregularities, while iron has concentrated towards the center ; it has gone with the copper.

It will further be observed that the minimum amount of each element is not found in the same sample for all. In sample No. 2 we have the minimum for silver and tellurium ; in No. 3 for gold and lead ; and in No. 4 for bismuth, antimony, and arsenic.

The blocks of copper represented by Figs. 2 and 3 were comparatively low in their contents of precious metals and impurities, while those in Figs. 5 and 6 were comparatively high. The sample represented in Fig. 7 is low in precious metals, and high in impurities ; yet we find that the silver has concentrated in accordance with the latter class. A general



Fig. 6.



Slag and Matte					
	536	532	603	604	613
	607	603	608	609	618
	605	608	612	613	616
	617	613	619	617	612

Fig. 7.—Black Copper.

furnace sample of this copper showed the following composition:

	Ounces.
Ag .....	62.2
Au .....	0.14
	Per cent.
Pb .....	0.78
Bi.....	0.0035
Sb .....	0.238
As .....	0.052
Te .....	0.0095
S.....	0.796
Fe .....	0.17

Fig. 8 is a photographic reproduction<sup>1</sup> of the face of *B* (Fig. 1) of the block of black copper represented in Fig. 6. It shows with the distinctness of a drawing each successive zone of solidification, by curved lines, or cavities, as well as the direction of solidification and concentration by straight linear cavities, which are perpendicular to the tangents of the curves, and which converge toward the center of solidification, the latter also being clearly indicated, much above the geometrical center, for reasons already given. The curved linear cavities were not readily discernible on the fresh cut, but were brought out plainly by rubbing with damp charcoal powder.

Reviewing the results obtained, they clearly prove the existence of two classes of copper-alloys. As already pointed out, in one class the foreign elements concentrate towards the center of solidification ; in the other the copper concentrates to the center, while the foreign elements appear to have concentrated towards the outside.

Not a single element tested for has remained homogeneously

<sup>1</sup> For the photograph the writer is indebted to Mr. William Keyser, Jr., of Baltimore.

throughout, but the degree of uneven distribution varies with each one.

From data given in Hofman's *Metallurgy of Lead*, pp. 244 and 245, I conclude that this metal shows the same characteristics, in this respect, as copper. Also from an article by A. Raht in the *Mineral Industry*, 1894, p. 414. This writer gives a few instances in which he shows that silver and gold in base bullion bars are highest at the bottom and sides and lowest towards the top. He quotes Rosenlecher (from the *Berg- und Hüttenmännische Ztg.*, Oct. 5, 1894) as having found exactly the reverse, and accuses the latter of strained figures, pet theories, etc. There seems no substantial reason for this inference, and undoubtedly Rosenlecher is as correct as Raht, and Raht as correct as Rosenlecher. The experiments of either covered but a narrow field, and neither discovered the other's side.

Very likely many of the alloys behave similarly, and homogeneity cannot be found with any of them.

Edward Mathey, in a publication in *Nature*, No. 1394, Vol. 54, calls attention to the fact that bars of gold, alloyed with zinc and lead, show very uneven distribution, gold having concentrated to the center and bottom, gravity being one cause.

To overcome difficulties in sampling such material, Mr. Mathey looks for a solvent and finds silver to be the medium. His figures cannot be pronounced as entirely conclusive, and the method proposed to obtain reliable samples is very circuitous, to say the least, although the trouble to be overcome is thereby minimized.

To come to the practical question of sampling, we must, from the stated and indubitable facts, draw the conclusion that it is almost impossible to obtain, from bars and pigs with irregular dimensions, by drilling, punching, or chipping, samples of satisfactory accuracy. As we have seen, concentration takes place from or towards every surface, and that in such bodies of metal a core, as it might appropriately be called, is formed, which is enriched or impoverished, as the case may be, and which in its shape does not conform to the outer surface. It is for this reason so difficult to obtain aliquot parts of the different portions of a bar or pig.

The root, then, of the difficulties of sampling, so often com-

plained of, lies in the irrational shape into which various metals are cast.

Another conclusion, which we must draw from observed facts, is the following : When we take from a molten mass of copper a sample by means of a ladle, the latter must be so hot as not to allow the forming of any solidified metal (sculling) ; for should this happen, the remaining liquid portion, which is to constitute the sample, would for one class of copper be too high in its contents of precious metals ; for the other class it would be too low. If we pour from a ladle, in which the whole metal is liquid, a so-called shot sample, there is no reason assignable that it is not a correct sample. When large samples of shot are taken from charges, which are supposed not to be homogeneous, they must, of course, be remelted, and a smaller sample taken in the same way ; or a sample plate must be cast, for which the rule below described must be observed, otherwise the final sample may become erroneous.

In most smelting and refining works sample-bars or cakes are desired, and to have these in the proper shape should be the duty of the sampler.

To eliminate all the difficulties inherent to pigs and bars, as above described, we only need reduce one dimension ; or to state it more plainly, we cast a plate, whose thickness is small, compared to the other two dimensions. Of course concentration in this plate is governed by the same law as in any other body ; it takes place from or towards the center, but the concentration in the horizontal direction, from the sides, can extend no farther than the distance equal to the thickness of the plate, for, when the solidification has proceeded that distance horizontally, the plate has entirely solidified vertically. We then have all around this plate a zone not wider than its thickness, where concentration has taken place just as in a bar or block ; that is, horizontally and vertically, and consequently, we have one enriched and one impoverished band around the four sides. In the part of the plate enclosed by this zone we have had concentration in the vertical direction only, and the plate here, therefore, consists of what we may term layers of metal of different concentration. If we drill or punch through all of these layers we obtain a correct sample of the whole plate. This then seems the simplest solu-

tion of the sampling of any metal or bullion, and it is difficult to see any reasonable objection to the casting into plates of appropriate size of such material destined for shipment, of which subsequent sampling is required, and for which the remelting and taking of samples from furnace charges is impracticable. Uncertainty in sampling would be eliminated, and giving the plates beveled edges the handling thereof would not be more difficult than with bars.

Fig. 9 represents a plate of refined converter copper, fifteen

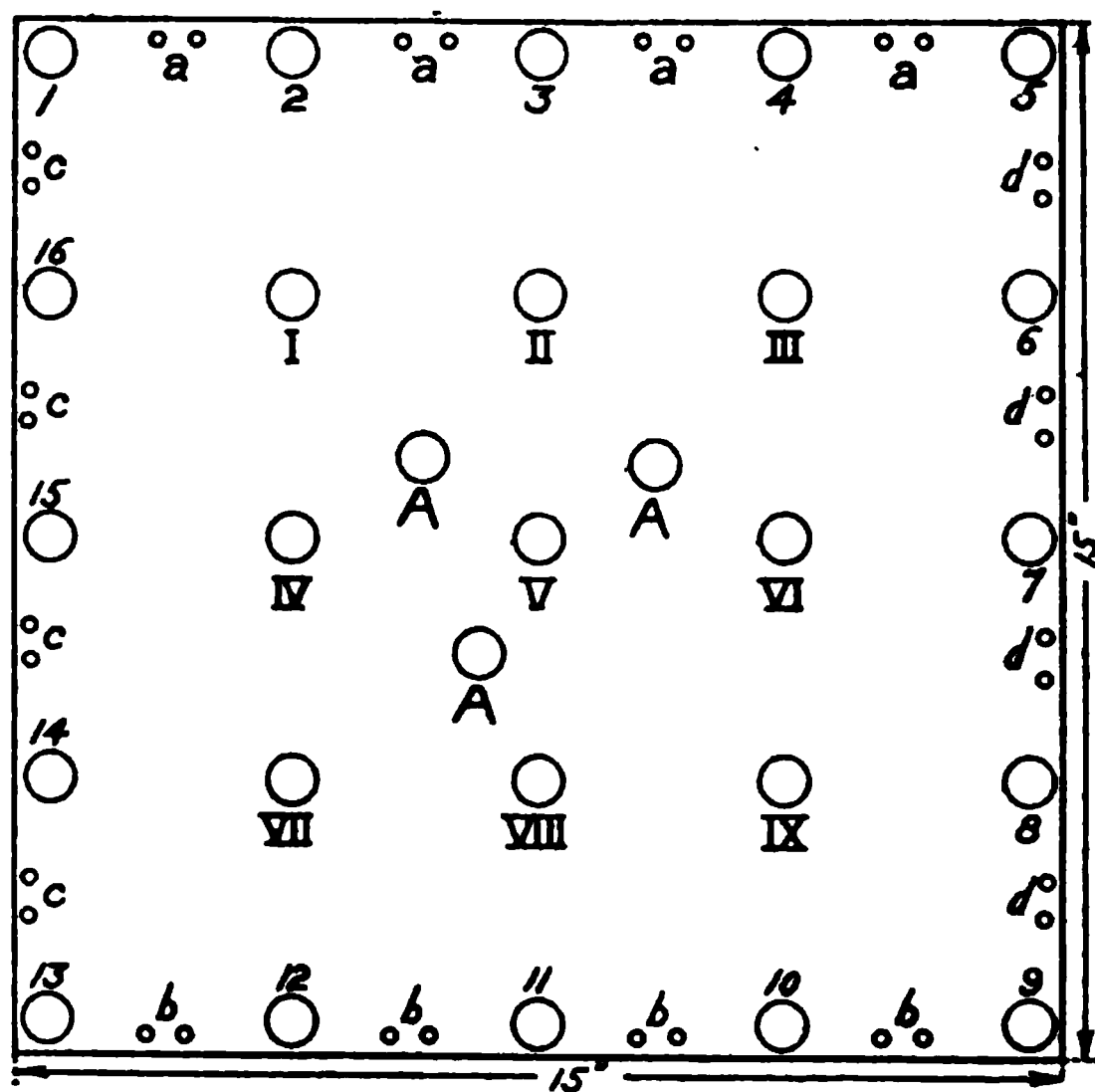


Fig. 9.

inches square by one inch in thickness. The holes designated by small letters were drilled with a one-quarter inch drill, one-fourth to one-eighth inch from the edge of the plate. The drillings from each side were collected in one sample, making the four samples, *a*, *b*, *c*, and *d*. The other holes were drilled with a three-quarter inch drill. Those designated by Arabic figures are from one-eighth to one-fourth inch from the edge. Those with Roman figures and the preceding ones were drilled through the plate. The three marked A were drilled about one-half inch deep, and the drillings collected for the top sample, then drilled through the plate, and the drillings taken for the bottom sample. The assays, in ounces per ton, were as follows:

$a = 105$ ,  $b = 100.7$ ,  $c = 101.7$ ,  $d = 100.1$ . Average = 101.9.

(1) = 99.2, (2) = 103.2, (3) = 104.2, (4) = 99.8, (5) = 98.6, (6) = 97.8, (7) = 98.5, (8) = 99.3, (9) = 98.7, (10) = 98.9, (11) = 99.4, (12) = 99.4, (13) = 98.9, (14) = 103.7, (15) = 98.5, (16) = 99.5. Average = 99.85.

I = 98.4, II = 98.8, III = 98.9, IV = 97.6, V = 99.6, VI = 99, VII = 98.2, VIII = 99.4, IX = 99.5. Average = 98.7.

A—top = 99.9, A—bottom = 98. Average, 98.9.

In the discussion of the theory of a thin plate it was pointed out that there must exist around the edge a zone of higher and one of lower concentration than in any other part of the plate, due to the horizontal and vertical movement of the molecules in this zone. The assays have demonstrated the correctness of that statement, although the zone does not appear to be strictly defined. This undoubtedly is due to temperature conditions of the mold and currents in pouring the metal.

The vertical concentration in the plate, inside the edge zone, is also clearly demonstrated by the top and bottom samples. These assays were repeated several times, while the rest were all made singly.

The samples and assays of the edge zone are, of course, incorrect representatives of the true contents of the plate and the furnace charge which it represents. The correct figure should be the average of I, II, III, IV, V, VI, VII, VIII, and IX = 98.7, as also the average of A-top and A-bottom = 98.9, the two figures being indeed very close together.

The plate, from which the above figures are derived, was cast

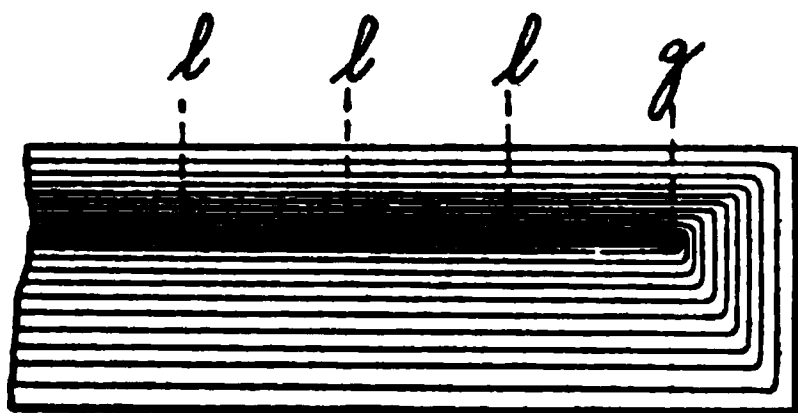


Fig. 10.—Vertical Section through the Edge and Part of Plate.

in a mold with very heavy bottom and thin sides. The solidification, therefore, took place much more rapidly from the bottom than from the sides and top. In Fig. 10 is illustrated this

process, it representing a vertical section through the edge and part of the plate. At *z* would be the highest or lowest point of concentration, according to the class of copper, the molecules meeting there from top, side, and bottom. At *l* would be the highest or lowest concentration of the layers, the molecules meeting from top and bottom.

For practical sampling, plates from eight to ten inches square are of ample size, but should not be more than one inch thick, and the drillings to be taken at least one inch from the edge through the entire plate.

After having seen how a correct shot sample or a reliable sample plate is obtained, let us now see how copper in its molten state is constituted.

The table below gives the results of tests, made for about three weeks, with furnace charges of from 90,000 to 110,000

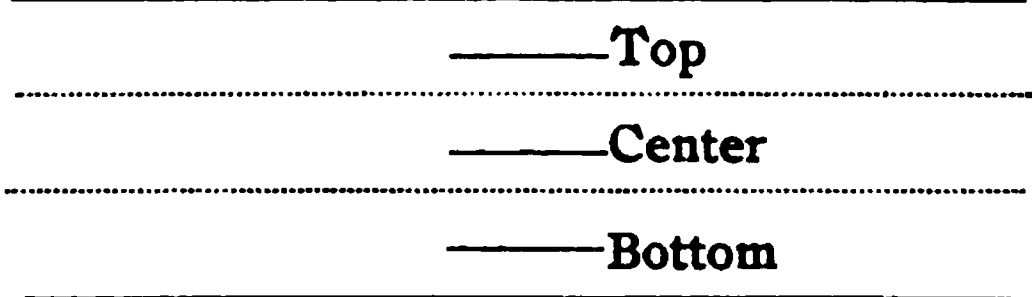


Fig. 11.—Position of Samples in Charge.

pounds of refined converter copper. The copper having been poled was, therefore, well mixed.

Sample plates were taken from the middle of every third of the charge, a practice adopted at these works. Fig. 11 illustrates the position of the samples in the charge.

	Ounces of sil- ver.	Average.	Ounces of sil- ver.	Average.	Ounces of sil- ver.	Average.	Ounces of sil- ver.	Average.
Top . . . . .	106.7	105.8	115.4	115.0	113.0	111.6	110.5	110.0
Center ..	106.5		113.9		111.8		109.7	
Bottom..	104.3		115.7		110.1		109.8	
Top . . . . .	110.3	109.9	109.1	108.7	109.3	108.8	108.2	108.1
Center ..	110.2		108.9		108.4		108.1	
Bottom..	109.1		108.1		108.7		108.1	
Top . . . . .	107.8	107.9	107.9	107.7	107.4	107.7	107.8	108.0
Center ..	107.9		108.6		107.9		108.2	
Bottom..	107.9		106.6		106.8		108.0	
Top . . . . .	108.1	108.1	108.5	108.5	106.8	107.0	105.8	106.4
Center ..	108.1		108.8		106.9		106.8	
Bottom..	108.2		108.1		107.4		106.5	
Top . . . . .	106.9	106.2	105.6	105.9	101.2	101.3	103.4	102.2
Center ..	106.0		106.2		101.4		101.8	
Bottom..	105.7		105.8		101.4		101.4	



The greatest irregularities occurred during the first few days, and were due to the furnace being new and the bottom seasoned with non-silver-bearing copper.

Each assay was made singly only and some of the differences may be attributed, therefore, to possible experimental errors, although nearly all are within the usual allowable limits in this kind of work.

The following are the values for silver and gold of three successive charges from a furnace of 30,000 pounds.

	Ounces of sil- ver.	Aver- age.	Ounces of gold.	Aver- age.
Top .....	163.6	163.1	0.24	0.24
Center .....	163.2		0.24	
Bottom .....	162.6		0.24	
Top .....	363.9	363.2	2.92	2.95
Center .....	363.3		2.96	
Bottom .....	362.5		2.96	
Top .....	319.9	320.0	2.32	2.35
Center .....	320.1		2.36	
Bottom .....	320.1		2.36	

On the strength of these results, it is safe to say, that any charge of molten copper, once thoroughly agitated and mixed, is, and remains, uniform, and a sample taken from any part correctly represents the whole charge.

The subject treated is not only of practical importance, but has also a very interesting scientific side.

It is of course nothing new to find uneven distribution of the elements in an alloy, but that this distribution should follow within very narrow limits the quantities of these elements present in two diametrically opposite ways, as shown by the preceding experiments, is a subject which has not been discussed, and which is decidedly perplexing to explain. No law known to the writer would apply to this remarkable phenomenon.

As shown by the analytical figures, the impurities, in the cases where they have concentrated at the center, have a far higher degree of concentration than in the cases where they have gone towards the outside. This is readily explained. In the first case, the molecules move in the same direction as solidification takes place. They are, therefore, able to move and concentrate until the last particle of the metal is solid.

By the increase of impurities towards the center, the melting-

point of the alloy in that region is undoubtedly lowered, and thereby the solidification retarded, thus giving the elements more time to pursue their course.

In the case of concentration towards the outside, the elements move in the opposite direction in which solidification takes place, and by encountering the already solidified metal, their course is ended. The center being drained of impurities, its melting-point undoubtedly rises, accelerating the process of solidification, and reducing the time of motion and concentration.

That each element shows a different degree of concentration has already been pointed out. In explanation of this fact it might simply be said that it is due to the differences of affinity, which, of course, is true. But for the term "affinity" between metals we have as yet no expression in values or figures. We shall, therefore, attempt to find whether there is any relation between this and other physical properties of the atom of the respective elements, and shall, for that purpose, first consider the case of the copper as represented by Fig. 2, the differences here being best defined.

In the following table the elements are arranged in the order of their degree of concentration.  $T$  = melting-point in  $^{\circ}\text{C}$ ;  $A$  = atomic weight;  $D$  = density, or specific gravity;  $V = \frac{A}{D}$  = atomic volume.

Element.	Concentration.	$T$ .	$A$ .	$D$ .	$V$ .
Pb .....	29.00	332	206.4	11.38	18.1
Bi.....	11.00	265	210.0	9.82	21.4
Fe .....	6.75	500	126.0	6.25	20.2
Sb .....	3.27	437	122.0	6.70	18.2
As .....	3.18	500	74.9	4.70 <sup>1</sup>	15.9
S.....	2.80	115	31.98	2.04	15.7
Ag .....	2.59	969	107.66	10.50	10.2
Au .....	1.60	1037	197.0	19.30	10.2
Cu .....	0.992	1057	63.3	8.80	7.2

Comparing the degree of concentration with the melting-point we find a correspondence in a general way, the elements of low melting-point showing a higher degree of concentration than those of high melting-point. The sulphur forms a very marked exception to this rule.

<sup>1</sup> This is the density given for amorphous arsenic; for the crystalline form it is 5.67; consequently  $V = 13.2$ .

Between degree of concentration and either atomic weight or specific gravity there seems to exist absolutely no direct relation. Gravity in this case, therefore, can be no factor governing the distribution of the elements.

Finally, in the last column, the values for the atomic volume unmistakably show a similar arrangement to those for concentration. From this fact a law can be formulated (in the way of suggestion) reading as follows: "When, on the solidification of a metal (copper) the small amounts of impurities segregate, or liquate, and consequently concentrate towards the center, the degree of concentration is greatest for those whose atomic volume, compared with the atomic volume of that metal, show the greatest difference." Influence of other properties (melting point, etc.) would modify the law accordingly.

If the law expressed be true, we should then have for that class of alloys an alloy series of the metals, in which the latter are arranged according to their atomic volume:

Element.	V.	Element.	V.	Element.	V.	Element.	V.
Ni.....	6.7	Rh.....	8.6	Au.....	10.2	Sn.....	16.1
Co.....	6.9	Ir.....	8.6	Al.....	10.7	Tl.....	17.1
Fe.....	7.2	Os.....	8.8	Cd.....	12.9	Pb.....	18.1
Cu.....	7.2	Pt.....	9.1	Mg.....	13.8	Sb.....	18.2
Pd.....	8.2	Zn.....	9.1	In.....	15.3	Bi.....	21.4
Ru.....	8.4	Ag.....	10.2				

The theory thus deduced from an alloy of copper is, in the main, corroborated by an analysis of lead bullion by Schertel.<sup>1</sup> Elements (Cu, Fe, Zn), whose atomic volume differ most from that of lead, have concentrated in a higher degree than those which stand closer to the latter. Antimony, which is almost identical with lead in this property, has concentrated with that metal. Silver and bismuth do not appear to fall exactly in line.

In the class of copper, in which the impurities are found concentrated towards the outside, the above rule does not seem to apply, but owing to the small differences in the degree of concentration and consequent large influence of possible experimental errors, it would be too venturesome to attempt the establishment of another rule or law.

One fact observed in the copper represented by Fig. 6 seems also confirmatory of the theory expressed; namely, the concen-

<sup>1</sup> Hofman's Metallurgy of Lead, p. 244.

tration of the iron with the copper, both metals having the same atomic volume.

The following table gives the elements and their degree of concentration, as found in the above-mentioned copper, compared with the other physical properties.

The degree of concentration was obtained by dividing the values of the fifth sample by those of the third.

Element.	Concentration.	<i>T.</i>	<i>A.</i>	<i>D.</i>	<i>V.</i>
Sb .....	1.39	437	122.0	6.70	18.2
Pb .....	1.21	332	206.4	11.38	18.1
Ag .....	1.21	967	107.66	10.50	10.2
Au .....	1.18	1037	197.0	19.30	10.2
Bi.....	1.17	265	210.0	9.82	21.4
As .....	1.12	500	74.9	4.71	15.9
Te .....	1.08	500	126.0	6.25	20.2
S .....	1.02	115	31.98	2.04	15.7
Cu .....	0.987	1057	63.3	8.80	7.2
Fe .....	0.79	2080	55.9	7.80	7.2

The material on the subject discussed is, as yet, too scant to allow the drawing of positive conclusions. It should always be remembered by investigators that to give their work full scientific value, not only one or two elements in a combination of many, should be studied, but the interrelations of all must be observed.

BALTIMORE COPPER WORKS, DEC. 1896.

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[CONTRIBUTIONS FROM THE CHEMICAL DIVISION, U. S. DEPARTMENT OF AGRICULTURE. No. 24.]

## RECOVERY OF WASTE PLATINUM CHLORIDE.

CONTRIBUTED BY H. W. WILEY.

Received January 26, 1897.

ALUMINUM turnings, freed of oil, have been used in this laboratory for some time for many purposes. Immediately after the publication of the paper of Wislicenus and Kaufmann<sup>1</sup> on the various applications of aluminum amalgam in the laboratory, a large quantity of these turnings was procured from the Pittsburg Reduction Co. Considerable difficulty was encountered in attempting to use these turnings in the manner described in the paper cited above. Mr. McElroy prepared the amalgam by washing aluminum clippings with ether to remove oil, treating with dilute caustic soda till free evolution of gas took place,

<sup>1</sup> *Ber. d. chem. Ges.*, 28, 1323.

and then washing with water to remove the alkali. The solution of corrosive sublimate was made in alcohol (chosen because the most convenient solvent), diluted with water, and poured over the aluminum. When the evolution of gas was seen to take place from every piece of aluminum in sight, the mercuric chloride solution was decanted and the aluminum washed chloride-free with water. The treatment with soda and mercuric chloride was then repeated. Finally the turnings were washed free of water with strong alcohol. The washed amalgam in fresh portions of "absolute" alcohol kept up a steady evolution of gas, long after the time all water should have been removed. A portion was removed from the alcohol, washed with ether, and placed in petroleum ether, where the evolution of gas became quite strong. The containing flask was loosely stoppered and stood aside over night. In the morning the petroleum ether was gone.

A fresh portion of amalgam from 200 grams of aluminum was prepared and treated as before, except that the washing with alcohol was more thorough. The alcohol was removed with ether and the amalgam finally washed with kerosene. It was then covered with kerosene and stood aside. In about half an hour the evolution of gas became quite violent and the containing bottle hot. On cooling under the tap the generation of gas slackened, but on standing increased again as the mixture warmed up.

The kerosene was such as is used for lamps. It gave a black zone of lead sulphide when treated with the lead acetate test. It is very likely Lima oil. As is well known in the Frasch process of purifying, the oil is passed through copper oxide, which it converts into copper sulphide. As for every atom of sulphur removed an atom of oxygen must go into the oil, probably the action of the aluminum consisted in appropriating this oxygen. Neither bright sodium or sodium amalgam had any special action on the kerosene used. The action of the amalgam on strong alcohol has been confirmed by Hillyer.<sup>1</sup> We have been able to use these turnings, amalgamated with mercuric chloride, for the reduction of nitrates to ammonia for analytical and other purposes, and it is probable that a speedy and accurate analytical process may be elaborated on this line. We

<sup>1</sup> *Am. Chem. J.*, 18, 621.

have, however, found the most successful use of the turnings in the recovery of platinum waste. This method of recovery is due to Mr. K. P. McElroy, and has been worked out by him in detail, and has been successfully used for some time in the recovery of platinum chloride waste from potash analyses. The method is as follows :

The waste platinum from potash determinations is collected and to the hot water solution of platinum potassium chloride is added aluminum in the form of clippings or turnings. In a few minutes a platinum-aluminum couple is formed and reduction goes on vigorously. The addition of hydrochloric acid is not necessary, but is advisable for promoting the settling of the platinum formed. After the reduction is complete, more hydrochloric acid is added to dissolve the excess of aluminum. When this is done the platinum will be found to settle and the supernatant liquid will be clear. The supernatant liquid contains but little suspended platinum, but it is passed through a large folded filter. If it does not come through clear, as is sometimes the case, return it a few times. As but little platinum gets on the filter, the same filter is used over and over again for successive filtrations until enough platinum accumulates to make its recovery worth while. When the clear liquid is all decanted, add water to the spongy platinum, shake, allow to settle, and decant. Repeat this until the supernatant liquid is free of chloride. The spongy platinum is then covered with strong nitric acid and heated for the purpose of removing copper. Aluminum often contains a little copper, which of course remains with the platinum. When the copper is all dissolved the copper nitrate and the excess of nitric acid are removed by washing with water by decantation as before, till the supernatant liquid is acid free when tested with Congo paper. The resulting platinum black is dissolved with aqua regia, made by mixing five parts of hydrochloric acid with one part of nitric, added in amount sufficient to dissolve all of the platinum present. The solution thus obtained is transferred to a porcelain dish and evaporated on a steam bath till a portion taken out with a rod solidifies on cooling. The residue is diluted with water and hydrochloric acid and re-evaporated. If, on adding water to the sirupy mass formed by this evaporation, nitrous vapors are

evolved, add plenty of water and re-evaporate. Repeat this evaporation with water till the nitrous vapors are no longer evolved on dilution. Finally dilute sufficiently to filter and add water until the color of a platinum chloride solution of known content is matched.

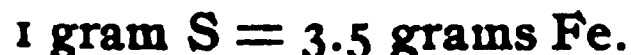
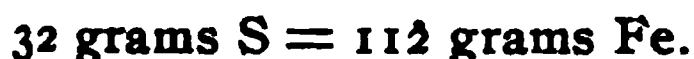
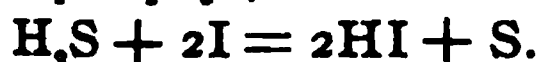
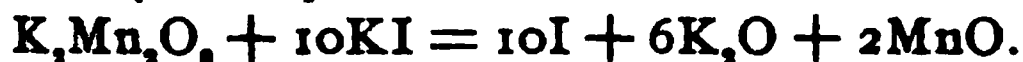
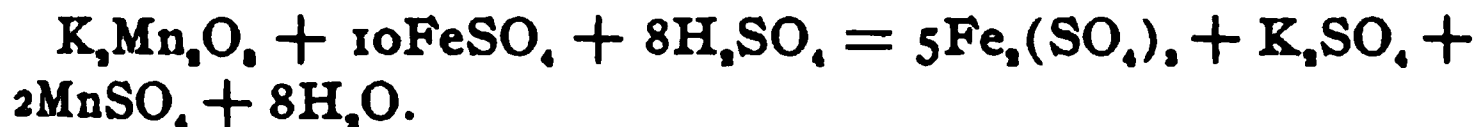
## STANDARD IODINE SOLUTION FOR SULPHUR DETERMINATIONS.

BY EDWARD K. LANDIS.

Received January 11, 1897.

THE following calculation shows an easy method of preparing Payne's iodine solution, with the least amount of calculation.

### REACTIONS.



When five grams are taken for analysis, 0.01 percent. = 0.0005 gram, and this multiplied by 1000 = 0.5 gram in a liter.

Let  $x$  = value of 1 cc.  $\text{K}_2\text{Mn}_2\text{O}_8$  in Fe in grams.

$$\text{Then } \frac{0.5}{x} = 0.5 \times \frac{3.5}{x} = \frac{1.75}{x}.$$

3.5

Therefore 1.75 divided by the value of one cc. potassium permanganate in iron in grams, gives the number of cc. of potassium permanganate to be added to the potassium iodide and sulphuric acid and diluted to one liter, to form iodine solution of such strength that one cc. will be equal to 0.01 per cent. sulphur when using five grams of sample.

### NOTE.

*Notes on "An Analytical Investigation of the Hydrolysis of Starch by Acids."*—A number of errors and misprints were overlooked by the authors in their compilation of this paper. The following are the most important:

<sup>1</sup> This Journal, 18, 869.

Page 873, ninth line, read " 77.40 " instead of " 76.40."

Page 873, second foot-note, read "Heron" instead of "Hearn."

Page 879, the equation for the curve of  $K_{\infty}$  is much more nearly:  $x^2 + y^2 - 758x + 772.4y = 0$ . The values of  $K$  as given in Table C are, however, correct.

Page 880, last equation should read  $m = \frac{\alpha + 141.5 K - 195}{26.52}$

By a clerical error the denominator 27.82 was carried through the calculations of Tables C and E. The values of  $m_{\infty}$  are, therefore, too low by 4.65 per cent. of the true value, the maximum therefore being 0.462 instead of 0.441. The values of  $g_{\infty}$  and  $d_{\infty}$  are correspondingly too high. This error does not affect the general conclusions of the article nor the character of the curves plotted in Plate B. The final resulting values of Tables I, II, and III, deduced from Table E, are moreover not materially changed by the correction.

Page 885, twenty-third line, the " $\alpha_{D_{\infty}}$ " should be " 131.7," the  $K$  (obtained) should be " 0.523," the  $K_{\infty}$  (calculated) should be " 0.533."

Page 885, third line from bottom read " possibly " instead of " possible."

Page 890, eleventh line, read " $\frac{1}{50} N$ " instead of " $\frac{1}{100} N$ ."

Page 890, Table II, Column II, read " 134.0 " and " 285.0 " instead of " 13.40 " and " 28.50."

Page 897, Plate I, the last plot should be five divisions to the right.

It is interesting to note that if there were but two simple carbohydrates resulting from hydrolysis, dextrose, and dextrin, as believed by some investigators,<sup>1</sup> the theoretical values of  $K$  would fall exactly on a *straight line* passing through the " zero " and " hundred " points of Plate A. The *experimental* values, on the contrary, show a maximum divergence from this line of about eight per cent., a discrepancy too great to be explained by experimental error or approximate specific gravity standard. Moreover, at the higher conversions, the curve approaches the value of pure dextrose again, showing quite conclusively that a body which we take as maltose, is an intermediate product between dextrin and dextrose, and not a decomposition product of dextrose, at least as far as the curve is carried.

<sup>1</sup> Flourens : *Compt. Rend.*, 110, 1204-1206.



Plots on a similar scheme made of the values of dextrin and maltose, present at successive stages of diastase conversion  $[\alpha]_{D_{306}} = 195$  and  $[\alpha]_{D_{306}} = 135.2$ , demonstrate that by the law of Brown and Morris,  $K$ ,  $m$ , and  $d$  can be graphically represented as straight lines.

Again it follows that the values of  $K_{\text{mix}}$  of a *mixture* of hydrolyzed starch products made by the action of acids must be necessarily less than the value of  $K$  of a homogeneous product of the same rotation, as it falls on the straight line joining the points on the  $K$  curve corresponding to the original values of the separate constituents.

A reprint of the paper on the hydrolysis of starch will appear in the *Technology Quarterly* in March. The authors will be glad to send corrected copies to any member of the Society interested in the subject.

GEO. W. ROLFE.

GEO. DEFREN.

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### NEW BOOKS.

COMMERCIAL ORGANIC ANALYSIS. BY ALFRED H. ALLEN, F.I.C., F.C.S. Second Edition, Revised and Enlarged. Vol. III. Part III. VEGETABLE ALKALOIDS (Concluded), NON-BASIC VEGETABLE BITTER PRINCIPLES, ANIMAL BASES, ANIMAL ACIDS, CYANOGEN AND ITS DERIVATIVES. xii + 508 pages. 1896. Philadelphia: P. Blakiston, Son & Co. Price, \$4.50.

This, the last volume but one of Allen's compendious work, is devoted to a study of the vegetable alkaloids, non-basic vegetable bitter principles, animal bases, animal acids, and cyanogen and its derivatives. It is really Volume V of the book, Volume III having grown into three large volumes during compilation and publication.

This volume, like its associates, is much more than its title indicates. It not only describes methods of procedure for the benefit of the analyst, but gives also a description of the various organic bodies, notes concerning their preparation and other encyclopedic matter valuable to the scientific reader.

Since Mr. Allen's work has so far outgrown its original plan, it might be well for him to consider the advisability of a re-arrangement of the material in a future edition in order to make it more convenient for different classes of chemical workers. For instance, in the present volume the matter on pages 1 to 166 is

of especial interest to pharmacists and toxicologists, pages 192 to 423 to physiological chemists, and pages 424 to 486 to manufacturing and technical chemists. The section embraced in pages 167 to 191 is of especial interest to chemists connected with the brewing industry. It is easy to realize, however, that the best arrangement of all the helpful matter which Mr. Allen has brought together is quite as much of a problem as the treatment of the subject-matter itself. Of the latter the previous volumes are witnesses of the great success which has attended the laborious and long-continued efforts of the author in culling from the scattered chemical literature of the whole world the facts and processes most useful to the busy worker in the various fields of chemical industry embracing the study of organic bodies. If it were possible to distinguish those organic bodies which are important from those of an opposite character, it might be said that Mr. Allen has included many things in his book which are not valuable from a commercial point of view. For instance, there is very little demand for adoninin, bilirubin, cevine, urinary deposits, euonymin, gall-stones, furze, hippuric acid, indican, jervine, kynurine, melan, nataloins, ophelic acid, piuri, rottlerin, quadri-urates, serpents' urine, taurocarbamic acid, urea, verine, and xantho-creatinin. These and hundreds of others are of so little commercial importance as to render questionable the utility of extending the volume to comprehend them. The description of these bodies would find a more fitting place in encyclopedias, kept for occasional reference, than in a practical manual to be consulted daily by the busy worker.

To the pharmacists the articles on the vegetable alkaloids will be found of useful interest. The physiological and agricultural chemists will welcome the articles on the potato, hops, and animal bases, the medical chemists the one on animal acids, and the manufacturing chemists the chapter on cyanogen.

It is doubtful whether asparagin, glutamin, betain, cholin and lecithin should be classed with the animal bases. These bodies are, first of all, products of vegetable metabolism, and their occurrence in the animal economy is quite as likely to be due to their ingestion in the food as to the results of any vital activity of the organs of the animal body.

The chapter on Hop Substitutes will prove of interest to American chemists and brewers at the present time, when so many of the State Legislatures, and even the National Congress are considering the subject of legislation looking to the definition of beer, and a description of its adulterants. We have in this country, as in England, no legal definition of beer, and in the absence of such a definition, the brewer using quassia wood instead of hops, could not legally be accused of practicing adulteration. In point of fact it is doubtless true that hop substitutes are used to a very limited extent in this country. Nevertheless, our chemists will be grateful to Mr. Allen for presenting in a succinct form the best methods of detecting the various bitter principles which have been proposed and used for hop substitutes. I am glad to see that he gives no credence to the absurd statement we all have heard, relating to the presence of strychnin in beer.

The article on urea is very full and complete, but inasmuch as the author has published a special treatise on urine analysis, and for the additional reason mentioned above, that urea has no great commercial importance, space would have been saved by its omission.

We shall welcome Mr. Allen's concluding volume, and the work when complete will find a place with that of Fresenius in the equipment of the analytical chemist. H. W. WILEY.

A BRIEF INTRODUCTION TO QUALITATIVE ANALYSIS. BY LUDWIG MEDICUS, Professor of Chemistry in the University of Würzburg. Translated from the Fourth and Fifth German editions, with additions by John Marshall, Assistant Professor of Chemistry in the Department of Medicine of the University of Pennsylvania. Fourth Edition. 203 pp. 8vo. Philadelphia: The J. B. Lippincott Co. Price \$1.50.

The writer of a book upon qualitative analysis at the present time finds it difficult to avoid following beaten paths. In fact, the methods given in the earlier text-books for the qualitative testing and separation of bodies have survived so many attempts to improve upon them, and the difficulties in the way of material innovations have usually proved to be so great, that it is hardly to be expected of an author that he should originate wholly new methods of qualitative work. Superior arrangement of topics, greater clearness and accuracy of details, and the presentation of known facts in such manner as to call for more vig-

orous exercise of the student's thinking powers constitute commonly the points of advantage claimed for any new book designed to replace older ones in elementary chemical analysis.

As regards accuracy, clearness, and mode of presentation, the English version of Medicus' book fulfils its purpose in a very satisfactory manner. The descriptions of processes are explicit and yet concise, and wherever possible are supplemented by tabulated statements. Useful data are given as to solubilities of precipitates. The rarer elements are separately treated in an appendix, and, for the further illustration of their reactions, analyses of their more important ores are described.

As regards arrangement, many teachers will find no objection to the book. The author's system of classification of bases is the same as that adopted in various other text-books, but this classification, according to which the metals precipitated by hydrochloric acid are treated first in order, as group one, and the alkali metals with magnesium are considered last, as constituting group six, has some disadvantages. The student on entering upon a laboratory course has much to learn regarding the nature of salts, and he gains a clearer idea of these if he experiments upon the compounds of the alkaline and alkaline earth metals before taking up the study of mercury, antimony, and tin. The greater simplicity in the reactions of the light metals is an additional reason why they should precede the heavy metals. The work of the translator has been well performed.

On account of its attractive form and its simple and clear directions and explanations, this book will prove a valuable aid to students of analytical chemistry. FRANCIS C. PHILLIPS.

LECTURE NOTES ON THEORETICAL CHEMISTRY. BY FERDINAND G. WIECHMANN, PH.D., Columbia College. Second edition. Revised and enlarged. xviii+288 pp. 1895. New York: John Wiley & Sons. Price, \$3.00.

The favorable reception accorded the first edition has led the author to issue a second edition of the "Lecture Notes on Theoretical Chemistry." The matter has been carefully revised and such additions made as serve to keep the student in touch with the most recent developments of chemistry, especially in the field of physical chemistry. The space given to stereochemistry

has been doubled and additions have been made to the excellent bibliography, which include important publications since the appearance of the first edition. The book is neatly printed and is quite free from typographical errors.

It is a matter of regret that in a revised work the subject of valence has not been treated differently. The classification of elements as artiads or perissads is unnecessary and misleading. While it is true that variations in valence usually proceed by twos, yet there are such well-defined exceptions, based upon vapor density determinations of the molecular weights of compounds, that we cannot feel justified in making the assumption that "two bonds neutralize each other." Indeed, does such an assumption really explain anything? Certainly, it is a questionable good when it leads to such illustrations as those used in the text to represent a monad, a dyad, etc. CHARLES H. HERTY.

PRÉCIS D'ANALYSE CHIMIQUE—(I) ANALYSE QUALITATIVE, pp. 190. (II) ANALYSE QUANTITATIVE, pp. 312. By E. FINK. Small 12 mo. Paris: Carré et Naud, Editeurs. 1896.

It is indeed refreshing to find a French chemistry which does not write water HO (in view of which we can pardon the continuance of Fl, Az, Bo, and St), and in which the reactions are uniformly well written and correct according to the modern standards. The French "devil," however, is responsible for many typographical errors, one of which deserves mention even in this brief review: "anhydride chromique" is metamorphosed into "anhydride chronique."

Part I is well done, the liberal use of different styles of type bringing the classification out clearly, the whole being put in good form for beginners to take hold of. It is regrettable that the chapter on dry tests was not made more complete, since it is well stated as far as it goes; the classification and treatment of the acids is particularly good. Part II cannot be so freely praised. The writer has attempted the impossible, even the undesirable. To condense the whole field of quantitative analysis into small space, is *necessarily* to sacrifice accuracy for brevity, to leave out all the fine points, to omit comparisons of methods and discussions of their limitations, and what kind of a chemist is he who is not taught these *from the beginning*? Such quantitative analysis as is put forth here, without criti-

cism of methods described, without the well-known precautions fully stated, would engender a chemist whose work would be of no value to himself or to anyone else. Part I will advance the true science of chemistry in France ; Part II will hinder it.

JOSEPH W. RICHARDS.

**STUDIES IN CHEMICAL DYNAMICS.** BY J. H. VAN 'T HOFF. Revised and enlarged by DR. ERNST COHEN. Translated by THOMAS EWAN, M.Sc., Ph.D. Large 8vo. vi + 286 pp. Easton, Pa. : Chemical Publishing Co. ; Amsterdam : F. Muller & Co. ; London : Williams & Norgate. 1896. Price, \$2.50.

Few works in chemistry have been more stimulating in their nature, and more productive of extended investigation of the most important character, than the simple, unpretentious "*Études de Dynamique Chimique*," which van 't Hoff published in 1883. It is a matter of general congratulation that a new edition of this work has appeared, and furthermore that it has been promptly issued in an English translation.

The volume before us possesses all of the attractions characteristic of its predecessor. It is not a text-book. It is simply an admirable monograph dealing with several of the most fundamental problems engaging the attention of the rapidly increasing number of chemists specially interested in the determination of the laws governing the rate of chemical change, the measurement of chemical affinity, and the general topic of chemical equilibrium. While these three subjects are not treated exhaustively, they are still discussed so fully that no better handbook could be used for guidance in the fields of research in question. The fullness of description, the ample details on apparatus for experimental investigation, the wealth of illustrations, the charms of the mathematical deductions, all render the volume simply invaluable, certainly for the beginner, and possibly for the more advanced worker in physical chemistry.

Some of the leading features of this new edition are : the recent work on the tartrates ; the discussion of Cohen's concentration cell ; the calculation of the change of solubility with the temperature ; the summary of all known methods for determining inversion temperatures ; the elaborate and instructive researches on the oxidation of aldehyde, phosphorus, and sulphur ; the many new data on the change of the equilibrium constant with

the temperatures ; the effect of pressure on condensed systems ; and the detailed discussion of the methods of determining the transition temperature.

It is to be regretted that several important phases of the general subjects have not been brought into discussion : the topic of catalytic actions ; the applications of the electrolytic dissociation theory to the phenomena of equilibrium ; the translator's own admirable work on the freezing-points of sulphuric acid solutions ; the author's extended investigations on dilute solutions ; and several others.

Here and there the need of more careful proof-reading is evident. The general typography of the book is, however, exceptionally fine, and the illustrations most effective. The fullness of the bibliographic features is particularly commendable. As we welcome so admirable an aid and guide to experimental work in physical chemistry, we cannot but regret that, thus far, there are so few centers in our own country, where the factors of experience, instrumental equipment, and enthusiasm combine to render America a noteworthy contributor in this field. Many indications, however, point to a rapid and early improvement in this respect.

THOMAS H. NORTON.

PRINCIPLES AND PRACTICE OF AGRICULTURAL ANALYSIS. BY HARVEY W. WILEY, Chemist U. S. Dept. of Agriculture. VOL. III, AGRICULTURAL PRODUCTS. xii + 665 pp. Easton, Pa.: Chemical Publishing Co. 1897. Price \$3.75.

This volume completes the most exhaustive work ever published on agricultural analysis. One of the sub-titles states that it is a manual for the examination of soils, fertilizers, and agricultural products. It is more properly a treatise on these subjects.

The volume under review is arranged in seven parts. Part I deals with the collection, preparation, and preservation of samples, the drying of organic bodies, the determination of ash, and the general description of the objects and methods of extraction by solvents. The full discussion of the subject of collecting and drying samples is timely and if the suggestions of the author had been more generally followed, the analyses of agricultural products that are found in various works of reference would have had a far greater value.



Parts II and III deal with the carbohydrates; Part II with sugars and starch in comparatively pure forms, while Part III deals with all carbohydrates in crude or manufactured products. These two parts comprise 250 pages and contain an enormous amount of information. Here the principles, as well as the practice, are well brought out. Numerous and extended tables of valuable factors are put where they are needed and the twenty-seven formulas for "Fehling's solution" will be appreciated by those who have had occasion to search chemical literature with only an author's name for a guide.

These sections include the more recent analytical methods for separation of the substances that are usually determined by difference and reported under the negative term of nitrogen-free extract.

Part IV is devoted to the examination of fats and oils. The physical methods are well represented while the best of the somewhat empirical methods for preliminary examination and identification of various oils and fats are very satisfactorily described and a good estimate of their comparative value is given. A considerable portion of this part of the work is devoted to descriptions of methods which are to be used in the examination of products that are more fully treated of in the last two parts of the volume.

The separation and estimation of bodies containing nitrogen which constitute Part V will prove of great interest and value to all chemists who are called upon to deal with animal and vegetable products. The results of much recent work on proteids are included here and the whole matter is presented in a far more satisfactory and systematic manner than is to be found in any other work in English.

The full treatment of the subjects in the first five parts enables the author to condense into less than eighty pages of Part VI an enormous amount of information on the subject of the examination of dairy products. Here we find all the important short cut methods for partial milk analysis and a very excellent discussion on the investigation of other dairy products.

If there is anything in the line of agricultural analysis that one cannot find elsewhere, he will find it in Part VII, which is devoted to miscellaneous agricultural products. Into 100 pages



is put a mass of explanations and directions for the examination of practically all agricultural products that, taken in connection with the previous volumes and parts of this work, constitute a veritable working library of agricultural analysis. The work is illustrated with many cuts, plates, and sections of apparatus, those on optical apparatus being especially full and clear.

There has been a slight tendency to criticise the work as being too full and as not pointing out select methods. The author forestalls this thought in his preface and must be congratulated on standing by his original purpose of presenting to the busy worker a broad view of a great subject.

The volume closes with the bouquet of fermented and distilled liquors, and no one will begrudge the author these delights at the close of his arduous and valuable work.

H. A. HUSTON.

**A MANUAL OF QUANTITATIVE CHEMICAL ANALYSIS FOR THE USE OF STUDENTS.** BY FREDERICK A. CAIRNS, A.M. Third edition, revised and enlarged, by ELWYN WALLER, Ph.D. New York: Henry Holt & Co. 417 pp. Price, \$2.00.

The unusual success that "Cairns' Manual of Quantitative Analysis" has won is doubtless largely owing to the attention given in it to the details of manipulation. It is not enough to tell a student of quantitative analysis what to do; he must be told how to do it. To write a book on this subject that will stand the test of laboratory use by students, one must be both a skillful analyst and an experienced teacher.

In the new edition, which has been largely rewritten by Dr. Elwyn Waller, several changes have been made. The chapters on "Proximate Analysis" have been cut out, and the scope of the work restricted to "Mineral Analysis;" a wise step, as the analysis of organic substances has been so largely extended, and has become a special subject with a literature of its own. Dr. Waller's excellent and useful paper on the "Properties of Precipitates" has been added, and the list of tables in the appendix has been increased. Under "Manufactured Irons" are described the colorimetric method for combined carbon, Stead's alkali method, Drown's method for silicon, the rapid volumetric method for phosphorus, Carnot and Drown's, and McKenna's methods for aluminum, and Lundin's method for arsenic. Under "Min-

eral Water'' Gooch's method for boric acid is given. Under ''Fertilizers'' the methods of the Association of Official Agricultural Chemists are quoted, and the Lewis-Thompson calorimeter is explained in determining the heating power of coal.

While to a professional analyst grammatical style may not seem of great importance, there can be no doubt about its importance to the student. He is frequently assured that accuracy of thought and lucidity of diction are characteristics of the truly scientific mind; but the vague, involved, and verbose style of more than a few of our chemical text-books cannot fail to make him doubt whether their authors possessed either accuracy or mental lucidity. In the present work, however, the clearness of the directions and the excellence of the grammatical style are worthy of commendation and imitation, while the printing and make-up of the book are creditable to the publisher. The new edition of the ''Cairns-Waller Manual'' will beyond a doubt be even more successful than the former one.

PETER TOWNSEND AUSTEN.

**ENGINEERING CHEMISTRY: A Manual of Quantitative Chemical Analysis for the Use of Students, Chemists, and Engineers.** BY THOMAS B. STILLMAN, M.Sc., Ph.D., Professor of Analytical Chemistry in the Stevens Institute of Technology. With illustrations. Easton, Pa.: Chemical Publishing Co. 1897. xxiii + 523 pp. Price \$4.50.

This volume will be found of great utility to the analytical chemist, and especially to him whose chief work comprises the examination of the materials of engineering. It contains a mass of most valuable data conveniently and compactly arranged, much of which is original and much of which was heretofore, for the most part, only to be found scattered through the files of periodical literature, or else in text-books relating to some special branch of the subject, and which has therefore only been available to the general analyst or to the chemical engineer as the result of more or less elaborate research.

Not only are described in detail nearly all of the conventional methods of analysis applicable to the various materials of engineering, such, for example, as the metals, alloys, cements, paints, oils, fuels, gases, water, etc., but many physical and mechanical tests in general use are clearly set forth, as, for instance, the mechanical testing of Portland cement, physical tests

of building stones, physical examination of lubricants, photometry, pyrometry, etc., and not the least valuable portions of this work are the elaborate examples which the author gives, showing methods of calculation whereby the results of analysis are utilized in practical work as, for example, in the calculation of blast-furnace charges, or in determining the heating power of fuels and gases.

While, as is to be expected, there is nothing particularly new in most of the processes given, many of them are more or less modified in some of their details which is doubtless due to the wide and varied experience of the author. It is to be regretted, however, that the description of some very valuable analytical methods which certainly should be included in a work of this character, are omitted, notably, for instance, the titration of iron salts with potassium permanganate, determination of  $\text{Pb}_2\text{O}_3$  in red lead, and the determination of the well known "saponification equivalent" in the analysis of oils.

The value of the work as a text-book for the instruction of students is to a certain extent impaired by reason of the fact that *theoretical principles* upon which the analytical processes are based are not sufficiently elaborated. This defect is, however, common to nearly all systems of instruction in analytical chemistry, especially in quantitative analysis, but does not to any extent impair the value of this book to the working chemist, although the system, upon which the subjects treated of are arranged, is susceptible of considerable improvement. The arrangement of the more complex methods in the form of "schemes," although not especially new is particularly worthy of commendation.

The volume is profusely illustrated and is furnished with a very complete table of contents and index, besides copious footnotes referring to original publications, as well as a large number of extremely useful tables, many of which appear to be original.

This book should find a place as a standard of reference in the working library of every analytical chemist and chemical engineer, and should, as it deserves, go through many future editions when such minor defects as it now contains will doubtless be corrected.

J. H. WAINWRIGHT.

## BOOKS RECEIVED.

**Commercial Organic Analysis :** A treatise on the properties, proximate analytical examination, and modes of assaying the various organic chemicals and products employed in the arts, manufactures, medicines, etc. By Alfred H. Allen, F.I.C., F.C.S. Second Edition, Revised and Enlarged. Volume III, Part III. Vegetable Alkaloids (concluded), Non-Basic Vegetable Bitter Principles, Animal Bases, Animal Acids, Cyanogen and its Derivatives. 1896. Philadelphia: P. Blakiston, Son & Co. xii + 508 pp. Price, \$4.50.

**Iron Making in Alabama.** By William Battle Phillips, Ph.D. Alabama Geological Survey, Montgomery, Ala. 1896. Jas. P. Armstrong, Printer. 164 pp.

**The Constants of Nature. Part V. A Recalculation of the Atomic Weights.** By Frank Wigglesworth Clarke. New Edition, Revised and Enlarged. 1897. pp. vi + 370. City of Washington: Smithsonian Institution. Price, \$2.00.

**A Simple Method of Water Analysis.** By John C. Thresh, M.D., D.Sc., D.P.H. 47 pp. Philadelphia: P. Blakiston, Son & Co., and London: J. & A. Churchill. 1897. Price, 88 cents.

**Notes on Assaying.** By P. de Peyster Ricketts and E. H. Miller. New York: John Wiley & Sons. viii + 311 pp. Price, \$3.00.

**The Carbohydrates of Wheat, Maize, Flour, and Bread, and the Action of Enzymic Ferments upon Starches of Different Origin.** By Winthrop E. Stone, Ph.D. Bulletin No. 34, U. S. Department of Agriculture. Washington: Government Printing Office. 1896. 44 pp.

**Laboratory Calculations and Specific-Gravity Determinations.** By John S. Adriance, A.M. Third Edition, Revised and Enlarged. ix + 144 pp. New York: John Wiley & Sons. 1897. Price, \$1.25.

**Notes for Chemical Students.** By Peter T. Austen, Ph.D., F.C.S. Second Edition. vi + 111 pp. New York: John Wiley & Sons. Price, \$1.50.

**Manures and Fertilizers.** (1) Report on the Enforcement of the Fertilizer Control Law. (2) Fertilizer Tests with Wheat. (3) The Waste of Farm Manures. (4) Green Manuring. Bulletin No. 34. University of the State of Missouri, Columbia, Mo. April, 1896. 35 pp.

**Précis d'Analyse Chimique.** By E. Fink. Première partie. Analyse Qualitative. 1896. 190 pp. Paris: Georges Carré, éditeur.

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Theo. S. Wornley

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**PROF. THEODORE GEORGE WORMLEY.**

BY EDGAR F. SMITH.

Received March 1, 1897.

ONE by one the men who contributed so materially in developing the science of chemistry in America are passing from among us. They have, for the most part, been men of broad training, who quietly, unostentatiously, but persistently, pursued some special line or branch of the science, and as a result of their untiring efforts have wrung from nature facts which possess not only a theoretical, but also practical value. In this band of earnest investigators and seekers after truth, none will deny a high position to him, whose name heads these lines.

As a member, councilor, and past vice-president of our Society his record may well claim our attention, while we pause to briefly note the lesson of his life and his achievements.

Little is known of the early days of Professor Wormley, other than that he was born in 1826 at Wormleysburg, one of the numerous villages nestling among the hills of that garden-spot of Pennsylvania—Cumberland County—the birthplace of so many men who have been powerful in affairs of the state and nation, as well as leaders in the various departments of learning.

His ancestors were Germans, who emigrated to America, as nearly as can be ascertained, about the year 1753. At what age the future professor left his native village for Carlisle, the seat of Dickinson College, remains unrecorded, but the records of that institution show that when sixteen years old (1842) he entered the preparatory department, where he

remained two years, when he was admitted to the Freshman class and continued in the regular course of study to the close of the Sophomore year. His name appears in the register of the College in the following year, but with the statement that he was pursuing a partial course.

Professor Wormley's vacations in these preparatory years were usually spent in scientific expeditions to the Western and Northern sections of the great state of Pennsylvania in pursuit of natural history studies. The leading spirit and guiding mind of these excursions was the late head of the Smithsonian Institution—Spencer F. Baird—then the curator of the museum and professor of Natural History in Dickinson College, "whose enthusiastic and unreserved devotion to science was calculated to awaken a deep interest in such studies \* \* \* and a number of young men, who afterward achieved eminence, received their first impulse from him." Of this number was Theodore Wormley, whose predilection for science studies was also encouraged, promoted, and greatly influenced by another Dickinson professor, Dr. William H. Allen, then professor of chemistry in the college, but subsequently the presiding head of Girard College.

This early preference for scientific investigation, no doubt, led Professor Wormley to choose medicine as his profession, so that after the customary year of preliminary reading under the preceptorship of Dr. John J. Myers, we find him matriculated in the Philadelphia College of Medicine, an institution not existing at present, but from which he graduated in 1849. Then followed a year's residence in Carlisle; after which he removed to Chillicothe, O., remaining there but a short time, when he proceeded to Columbus, O., where the practice of his profession was begun. His first professional appointment came in the year 1852, when he was elected to the Chair of Chemistry and Natural Science in The Capitol University, located in Columbus, O. This position he held until July, 1865. While holding this Chair he also held the professorship of Chemistry and Toxicology in Starling Medical College, to which he had been elected in 1854, and from which he resigned after twenty-three years of most satisfactory work. The hours not devoted to teaching or research were occupied in the discharge of appointments, for



which his qualifications admirably fitted him, such as State Gas Commissioner of Ohio (1867-1875), and Chemist of the Geological Survey of Ohio (1869-1874). In both these positions Professor Wormley rendered most distinguished service, as is amply evidenced by the various State Reports in which his records are published.

His acknowledged reputation among medical men as a teacher and toxicologist led to his election, on June 5th, 1877, to the Chair of Chemistry and Toxicology in the Medical Department of the University of Pennsylvania, becoming thereby the direct and worthy successor of such eminent men as Benjamin Rush, James Hutchinson, James Woodhouse, J. Redman Coxe, Robert Hare, and Robert E. Rogers. And here he continued until the morning of January 3rd, 1897, when the final summons came, and the earnest, ever-active master laid aside the working tools of life to penetrate the veil which separates us and the present from the great hereafter.

For forty-five years Professor Wormley taught and investigated. The results of his researches appeared under the following titles:

1. On Some of the Chemical Reactions of Strychnia. Chem. News, 1860.
2. Notes on Some of the Chemical Reactions of Atropine. Chem. News, 1860.
3. Notes on Some of the Chemical Reactions of Brucine. Chem. News, 1860.
4. Chemical Reactions of Corrosive Sublimate. Chem. News, 1860.
5. Chemical Reactions of Morphia. Chem. News, 1860.
6. Chemical Reactions of Narcotine and Meconic Acid. Chem. News, 1860.
7. Nobert's Test Plate and the Striae of Diatoms. Chem. News, 1861.
8. Quantitative Estimation of Urea. Chem. News, 1882.
9. Recovery of Absorbed Morphine from Blood. Chem. News, 1891.
10. A Contribution to Our Knowledge of the Chemical Composition of Gelsemium. Am. J. Pharm., 1870.
11. Alkaloids of Veratrum Viride and Alum. Am. J. Pharm., 1876.
12. Preparation and Toxic Effects of Gelsemia. Am. J. Pharm., 1877.
13. Reinsch's Test Fallacies. Am. J. Pharm., 1880.
14. Constitution of Gelsemium. Am. J. Pharm., 1882.
15. Some of the Chemical Properties of Mydriatic Alkaloids. Am. J. Pharm., 1894.
16. Tests for Quinine. Am. J. Pharm., 1894.
17. Recovery of Absorbed Morphine from the Urine, the Blood, and the Tissues. Univ. Med. Mag., 1889-90.

18. Concordant and Micrometric Measurements. Univ. Med. Mag., 1890-91.

19. Chemical Analysis of Coals, Iron Ores, etc. Ohio Geol. Survey, 1870.

Editor of the Ohio Medical and Surgical Journal, 1862-1864.

These in a measure indicate the direction of his activity, but the lasting monument which he raised to science and his own glory is his grand work entitled "Micro-Chemistry of Poisons." In it are embodied the records of thousands of the most painstaking observations. The patience displayed in the preparation of this volume of world-wide reputation—the recognized authority in all lands—is marvellous. It is interesting also to note that in this, his greatest effort, he was assisted by his devoted wife, who learned the art of steel engraving solely for the purpose of delineating upon steel nearly one hundred exquisite illustrations of crystals, drawn directly from the object as observed under the microscope.

A marked characteristic of all work done by Professor Wormley is its extreme accuracy. In searching for the truth, time and labor ceased with him to be factors. Repetition was practiced to an almost painful degree. Every subject was studied from all possible points of view, so that in his special field it is not in the least surprising that he was early recognized as an authority and expert.

As a teacher he ever maintained a high rank. His power of imparting knowledge was equaled by few. That patient spirit which dominated all his work manifested itself here and is evidenced by thousands of students to-day. Details were presented with care, and every effort was made to have even the dullest neophyte understand. It was ever the aim of the professor to have the principles of the science thoroughly grasped and comprehended by his pupils. Superficiality he despised. Thoroughly conversant with his subject, he possessed the power of presenting it in an extremely lucid manner.

Though modest and retiring to a degree, Professor Wormley was the recipient of many honors, and received elections to many scientific societies. Thus he was one of the Vice-Presidents of the Centennial of Chemistry, held in Northumberland, Pa., in 1874; a member and Vice-President of the American Chemical Society; a member of the American Philosophical Society; a member of

the American Metrological Society; a corresponding member of the New York Medico-Legal Society; a Fellow of the College of Physicians, Philadelphia; a Fellow of the American Association for the Advancement of Science, and a Fellow of the Chemical Society of London.

In 1870 he received the honorary degree of Doctor of Philosophy from Dickinson College, and the same degree from Pennsylvania College in 1877, while Marietta College, Ohio, conferred upon him the degree of Doctor of Laws in 1870.

Personally Professor Wormley was a modest, unassuming man. Few knew him well. Those who were fortunate enough to brush aside the mantle of reserve which usually surrounded him, found a genial, kind, sympathetic companion, with a mind stored with the most varied knowledge and ready to unfold itself to those who had won his confidence. In his comments upon the work and writings of others he was extremely considerate. No bitter criticism was ever allowed to pass his lips, no matter how widely the views set forth by their authors may have differed from what he believed to be correct. True, upright and just in his dealings with all men, it is not surprising that he won the hearts of the great student body and of all with whom he came in contact. By them his memory will ever be cherished as one who loved and sought the truth alone, who was content in the quiet of his laboratory, away from the noise and bustle of the world, to work out the facts, which as we find them arrayed in his great work, will cause future students of chemistry to render to his name that homage which ever falls to the master in any great effort.

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## NOTES ON CAFFEIN.

BY G. L. SPENCER.

Received January 13, 1897.

**S**HORTLY after submitting the above title to the Secretary, the November, 1896, number of the Journal was received, which included a paper on the estimation of caffein. This paper in many respects anticipated the notes I intended submitting to the Society.

It was my intention to discuss some of the statements of Gomborg<sup>1</sup> in his paper describing his volumetric method for caffein,

<sup>1</sup> This Journal, 18, 331.

using Wagner's reagent. Gomberg cites certain experiments in which he secured but a small proportion of caffein present in a certain sulphuric acid solution of the alkaloid, even after shaking many times with chloroform. The experience of Allen,<sup>1</sup> or Puckner,<sup>2</sup> and my own work all demonstrate that the caffein may practically be entirely removed from water solution by shaking four or five times with chloroform. However in a number of instances I detected a trace of caffein by the "murexid test," and in later work by Wagner's reagent, as recommended by Gomberg, in the watery residue, left after five extractions with chloroform. In view of this fact and the frequent necessity of slight acidulation of the solutions with sulphuric acid to reduce the tendency to the formation of obstinate emulsions, the writer deemed it advisable, for precautionary reasons, to recommend seven extractions, in the publication of the gravimetric method<sup>3</sup> from which Gomberg quotes in his paper. Unless great care is observed in the gravimetric method in the recovery of the chloroform by distillation, an error may result from the entrainment of caffein with the chloroform vapors. A safety bulb, such as is made for use in the Kjeldahl nitrogen process, effectively prevents loss of caffein in the distillation.

It is difficult in the gravimetric method to obtain an absolutely pure caffein, there being usually sufficient foreign matter present to give a slight coloration in the cold with concentrated sulphuric acid. This contamination with foreign matter is probably too slight to appreciably affect the accuracy of the results. The two methods give almost identical results as shown by the following examples. The same purified solution was used for each of the methods:

Description of samples.	Gravimetric method.	Gomberg's method.
1. Mixed tea.....	2.24	2.21
2. Japan tea dust .....	2.27	2.28
3. Japan tea dust .....	2.29	2.30

The following method of purifying the caffein was tried with Sample No. 3 with a promising degree of success: Five grams of the finely ground tea were boiled thirty minutes with approximately 400 cc. water; a considerable excess of recently prepared

<sup>1</sup> Commercial Organic Analysis, 3, Part II, 485.

<sup>2</sup> This Journal, 18, 978.

<sup>3</sup> J. Anal. Chem., 4, 390.

ferric hydroxide was added, and after digesting about one hour, the mixture was cooled and transferred to a graduated flask and diluted to 500 cc. An aliquot part of the solution was filtered off and treated by Gomberg's method. The difficulty experienced was in filtering off the periodide of caffein. The percentage of caffein obtained was 2.28, as compared with 2.29 and 2.30 by the other methods. The solution of caffein obtained by this method is not sufficiently pure for the extraction of the alkaloid by chloroform for analytical purposes.

In comparative experiments with a number of methods for the determination of caffein in teas, the Gomberg method has given the most satisfactory results and admits of wider application than the gravimetric methods.

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## **SOME APPARATUS FOR THE TECHNICAL ANALYTICAL LABORATORY.**

BY EDWARD S. JOHNSON.

Received February 1, 1897.

**T**HOSE branches of chemical industry which are dependent in part for guidance upon an analytical laboratory are each year becoming more exacting in regard to their demands upon the laboratory for accurate, yet rapid, work in large quantity.

Besides stimulating research with a view to shortening established methods of analysis, or the invention of new ones requiring less time for their execution, this exaction has resulted further in the introduction of much special apparatus for expediting the routine operations of the laboratory. A visit to any of the well-conducted technical laboratories of the day will show that much work of this sort has been done, and the frequent contributions on the subject in the contemporaneous journals of chemistry give evidence that activity in this direction is not abating.

It is the purpose of the present communication to present a few forms of apparatus designed in the first instance to facilitate and hasten the work of the technical laboratory with which the writer is connected. The efficient service which these devices have rendered induces him to venture upon their description with the thought that it may prove of interest to others engaged in the same field of work—the analysis of iron and steel. Although more particularly adapted to the special work mentioned, the ap-

paratus, in some cases, may perhaps be found capable of advantageous application in connection with other branches of technical analysis, and possibly, in one or two instances, in the general analytical laboratory. In its application it concerns the operations of: I. Measuring Reagents; II. Filtration; III. Solution with the Aid of Heat.

#### I. MEASURING REAGENTS.

As is well known, the technical analyst is constantly required to treat a large number of samples or solutions successively with a given quantity of some liquid reagent in order to obtain a solution, effect a precipitation, etc., *where great accuracy is not important*. Such manipulations may be speedily executed by the simple arrangement shown in Fig. 1.

A reservoir of several liters capacity, containing the reagent, is connected by a siphon with a measure, and the whole mounted upon a stand with castors. The stand *S* is of finished oak, and ten to eleven inches in height. In its top there is a shallow circular space slightly larger in diameter than the reservoir *R* which, in this case, is a four-liter bottle. This sufficiently secures the reservoir in its position on the stand. The bottle is closed by a rubber stopper into which two glass tubes are inserted, *T* reaching to the lower surface of the stopper, and *M*, of one-quarter-inch tubing, which extends to the bottom of *R* and forms the siphon connecting with the graduate. The latter is provided at both ends with accurately ground stop-cocks. At *V* is a vent through which air escapes or enters as the graduate is filled or emptied. In the upper end of the measure and directly under the opening in the stop-cock, a short piece of tubing is fused. It directs the liquid as it enters the measure, preventing its running down the walls and consequent escape at *V*. A clamp attached to a stout wooden peg fixed in the under side of the top of the stand holds the graduate firmly.

Until the supply of reagent in the reservoir is exhausted, the apparatus is clearly ready for continuous service after the filling of the siphon. This, plainly, may be done either by applying pressure through *T* or suction at *V*, the lower stop-cock being first closed. When used it is drawn to the edge of the work-table, where the graduate projects slightly, and the reagent may be conveniently delivered into the vessels destined to receive it.

Fig. 2.

1

Fig. 1.

Fig. 4

Fig. 3

1  
2  
3  
4  
5



5-1012

1

Fig. 6

As the level of the liquid in the reservoir falls, the rapidity of the flow from the siphon of course decreases. Should the delivery become too slow, a force-pump (rubber bulb with valve) may be used to restore the failing pressure. When this addition is made, it is convenient to attach a piece of rubber tubing with a pinch-cock at *T*. It allows of quickly relieving the pressure within the reservoir. A third tube bent like *T*, but having a small bulb in the outer shank, connects with the pump. The bulb is filled with cotton which filters the air forced through the tube. Where reagents contain solids in solution, it is usually necessary, to avoid the sticking of the stop-cocks, to clean them and the graduate directly after using, especially when some time must elapse before the apparatus is again used.

In some analytical work, it is desirable to be able to deliver larger volumes (200 to 250 cc.) than is possible with the arrangement just described. This, however, is easily adapted to the work indicated. The height of the stand remains the same. The reservoir has the same capacity, or may be larger, according to the demand made upon its contents. *M* may be of somewhat larger diameter with advantage; it no longer acts as a siphon, and merely connects reservoir and measure. The measure with its increased capacity is much longer than before, and is so placed that the outer end of *M* is above the level of the liquid in the filled reservoir. The upper stop-cock may then be dispensed with, as the graduate is filled by means of the force-pump and the flow of the reagent from *M* may be instantly stopped by opening the valve (rubber tubing with pinch-cock) which is added at *T*. This and the pump, conveniences in the form of the apparatus seen in the figure, now become necessities.

By substituting for the graduate a burette, an extremely practical combination is obtained for *measuring small volumes accurately*. *M* must be made higher and dips about one inch into the burette without being attached to it. A disk of soft rubber with a hole to allow the passage of the tube, closely covers the mouth of the burette. Further, a second clamp is needed to retain the burette in a vertical position. It grasps the neck of the bottle at one end and the burette at the other, and is a simple adaptation of a familiar form of clamp. The filling of the bu-

rette, as need hardly be remarked, is conducted exactly as described for the arrangement with the larger measure.

This modification of Fig. 1 was devised for use in connection with the colorimetric determination of carbon in steel. It has so effectually aided in the work that it now seems almost indispensable. It is necessary for obvious reasons to do the work referred to in the draft-chamber. When not in use, the appliance must be kept out of the way of other apparatus and work, usually back against the wall of the chamber out of easy reach for service. The facility with which it may be moved to a convenient position when needed becomes here an especial advantage.

## II. FILTRATION.

1. *Filtering Apparatus with Automatic Feed.*—For certain phases of the routine work of the technical laboratory, the necessary reagents require preparation in large quantities as an economy of time. This involves, as a rule, the filtration of solutions several liters in volume. With the device seen in Fig. 2, readily constructed from materials always at hand in the laboratory, such filtrations are rapidly executed with extreme convenience. Of the two bottles shown in the cut, the one on the right contains the unfiltered solution, while the other receives the filtrate and carries the filter noticed in the funnel held by the rubber stopper in the neck of the bottle. The filter is of thick felt formed from paper or asbestos pulp upon a perforated porcelain filtering-plate.<sup>1</sup> The funnel is about four inches in diameter and has a carefully ground edge. For most purposes, a plate one and a half to two inches in diameter will answer. Resting on the funnel with the filter is a second inverted one of the same diameter, also having a ground edge, and with a long stem bent to reach to the bottom of the bottle containing the solution to be filtered. A ring of soft rubber *R*, between the funnels, and their ground edges effectually secure an air-tight joint when external pressure is applied. It was first intended to use funnels with quarter-inch flanges as a means of fitting them together. The

<sup>1</sup> O. N. Witt : *Ber. d. chem. Ges.*, 1886, 918. This exceedingly useful form of filter in the preparative work of the laboratory, particularly the organic laboratory, whether it be desired to clear a solution or collect a precipitate, has recently been used in my laboratory with advantage in certain *quantitative work*. By means of the pulp-filter, tungstic hydroxide, for instance, a most troublesome precipitate to handle in large quantities, may be collected and washed with little difficulty.

above simpler arrangement, however, as intimated, works perfectly. The end of the stem of the upper funnel has a lateral opening,<sup>1</sup> obviously that the solution may have unhindered entrance.

The preparation of the filter (making the pulps and forming the felt upon the plate) needs no explanation. When asbestos is used it should first be ignited. The fibers then become somewhat elastic and produce a spongy, rapid filter. The felts are usually three-eighths to one inch thick, according to the difficulty of the filtration, the thicker felts being used for the more obstinate cases.

The filtration is begun, after placing the parts of the apparatus as seen in the figure, by starting the filter-pump. The bottle to receive the filtrate and the space enclosed by the funnels, as a result, are partially exhausted of air. The external air-pressure now being considerably greater, the funnels are pressed forcibly together. The solution to be filtered rises and flows upon the filter, the flow continuing only as fast as liquid is withdrawn; the solution is thus automatically fed to the filter. The apparatus requires no further attention until the filtration is complete.

2. *A Revolving Filter-Stand*.—This device is represented by Fig. 3. The tripod base carries a vertical steel rod about three-eighths of an inch in diameter and eight inches high. Its free end is rounded and forms the pivot for the rest of the apparatus. This consists of a central column of brass and two disks of oak, each of three crossed layers. The column fits closely over the steel rod, and is one inch in diameter and fourteen inches high. On its lower end is a broad flange to which the larger disk is attached. The disk is nineteen inches in diameter and one inch thick, including the rim which projects about one-quarter of an inch. The upper disk is ten and one-half inches in diameter and one-half inch thick. It contains fifteen tapered holes on the circumferences of an outer and inner circle, twelve in the outer and three in the inner. The holes are about one and one-quarter inch in diameter on the upper side of the disk. Screwed to its under side is a flanged brass collar with set-screw, by which its height on the column may be adjusted. Both disks are well finished and protected against moisture by outside varnish.

<sup>1</sup> Made by blowing a bubble in the tube at the desired point, rubbing it off, fusing the edge of the opening left, and cutting the tube through the center of the hole.

When in use, sheet rubber covers are placed on them as a further protection. At *S* is a swivel with a clamp. It serves to hold the rubber tube through which liquid is supplied from an elevated reservoir for washing the precipitates and residues collected upon the filters. Through a small hole in the swivel at the base of the holder, the steel rod bearing the column and its disks may be oiled.

The stand, as described, was designed especially for handling the large number of ammonium phosphomolybdate precipitates obtained from the phosphorus determinations of the steel works' laboratory. The beakers are No. 1 Griffin's and the funnels two inches in diameter. Three of the fifteen beakers with which the stand may be used are placed upon the upper disk during the filtration.

### III. SOLUTION WITH THE AID OF HEAT.

1. *Solution in Large Test-Tubes.*—In Fig. 4 is shown an apparatus<sup>1</sup> devised for use in the colorimetric determination of manganese in steel. The part of the process here concerned involves the solution of the sample in nitric acid, heating the solution to boiling, and the oxidation of the manganese it may contain to permanganic acid by continuing the boiling after the addition of lead peroxide. The samples are dissolved in ten-inch by one-inch test-tubes, eight solutions being made at once. The tubes are supported in a vertical position by a set of equi-distant clamps, modifications of a well-known form of spring-clamp. They are of stiff sheet brass, as regards the jaws, and their shafts screw into a central cylindrical block of the same material. The whole revolves about the three-eighth-inch vertical brass rod of the tripod-stand, and is supported by a similar block which may be fixed at any point on the rod by the usual set-screw. Below the clamps are eight Bunsen burners, radiating at angles of 45° from a short hollow cylinder which distributes gas to the burners. Their position on the axis is also adjustable. The burners are provided each with a stop-cock and chimney. The manner of attaching the chimney is shown at *C*. To protect the apparatus from the corrosive vapors to which it is constantly

<sup>1</sup> Made by Messrs. Bullock & Crenshaw, of Philadelphia, to whom credit is due for the careful execution of the idea of the apparatus as conveyed in a somewhat crude sketch prepared during the hurry of remodeling and re-equipping a laboratory. The heating apparatus shown in Fig. 5 was also constructed by the same firm.

exposed, it is varnished with special care: the polished brass parts with coach-varnish, the iron base and copper chimneys with asphaltum varnish.

By the above construction and adjustments, the solutions in the test-tubes may be brought almost simultaneously to boiling, and further treated as already pointed out. To arrest the boiling of the solutions, a slight movement of the set of clamps to the right or left suffices; if it be desired to remove only a part from the action of the flames, the tubes are drawn up in the clamps as shown in two instances in the cut.

2. *Solution in Dishes, Beakers, and Flasks.*—A few remarks of explanation in connection with Fig. 5 will make plain the construction of the apparatus here referred to. A rectangular iron stand nine inches high, twenty-five inches long and eighteen inches wide forms its framework. This is built of an upper and lower frame, joined by legs of half-inch round bars. Low down on the legs is the lower frame, consisting of two end-pieces through which the legs pass, and three similar bars at right angles to the end-pieces. The bars of the frame are about one inch by three-sixteenths in size. Its parts are substantially riveted together. Within slight limits it may be given a higher or lower position. Screwed into each of the longer bars are four Argand burners with four-inch clay chimneys. The burners are connected by rubber tubing with the stop-cock of the one-inch brass pipe attached in front to the legs of the stand. The manner of connecting the tubing with the burners is best seen in the case of the middle row. Through the pipe in front, from either end, and its stop-cocks, gas may be supplied to any one, part, or all of the burners. The first, fourth, seventh, and tenth stop-cock, counting from the left, connect with the rear row of burners; the second, fifth, eighth, and eleventh with the middle row, etc.

The upper frame, above the burners, bears a loose asbestos pad, which forms the top of the stand. It is rimmed with sheet copper and has twelve two-inch holes, each directly over a burner. Two cross bars in the frame, parallel to those in the lower frame, prevent a sagging of the pad.

The feet of the stand are shod with rubber (stoppers bored partially through with a cork-borer) for an apparent reason.

To subserve the occasional cleaning and revarnishing to

which the apparatus, used as it is in the corroding atmosphere of the draft-chamber, must be subjected, the burners, as implied above, can be easily removed, and the gas-pipe in front detached from the clamps which support it. Besides hastening solution, this device may also be used with advantage for certain evaporations and other operations which at once suggest themselves.

The compactness of the apparatus, the ease with which the flames are perfectly controlled, due to the position of the stop-cocks, and a definite plan in their connection with the burners, the varied application of which it is capable, and its convenient portability combine to make it a most useful appliance in the laboratory.

3. *An Apparatus for Use in the Determination of Sulphur in Steel by the Evolution Method.*—Although excellent forms of apparatus have been proposed for the purpose indicated, a description of the combination shown in Fig. 6 is nevertheless undertaken, it seeming to the writer to have advantages which apologize for its addition to the already numerous list which might be compiled from the literature of the subject.

That part of the familiar method for the determination, which the present apparatus was designed to execute, consists in dissolving the sample of metal in hydrochloric acid, and the passage of the gases formed through an ammoniacal solution of cadmium chloride. The contact of acid and metal results at first usually in a brisk evolution of gas. This, however, soon slackens, and is then restored to the desired moderately rapid rate by the application of heat. As the metal dissolves, heating fails to maintain a steady flow of gas. At this stage of the process, hydrogen is forced into the flask in which the solution is now nearly completed, and next heated to boiling. The hydrogen serves (as need scarcely be remarked) a double purpose: the residual gases in the flasks are driven rapidly into the cadmium solution, and the liability (especially when the attention of the analyst must be divided among a number of simultaneous determinations) of the latter's "striking back" into the flask, during the boiling, is entirely obviated.

The following references to the figure will make plain the relation of the parts of the arrangement shown by it to each other and the manipulations thus roughly sketched.



The 250 cc. flasks *F*, in which the metal and acid are brought in contact, stand upon a light iron table nine inches high, seven inches wide, and twenty-three inches long. The top of the table is of asbestos board as in Fig. 5; under each flask, there is a two-inch hole through which, obviously, heat is applied to the flasks from the burners below. A stop-cock at one end of *G* enables the regulation of the supply of gas to all the burners. It is, however, essential for apparent reasons, to be able to perfectly control the supply to each burner separately. This has been effected, not by the use of the customary stop-cock, but by a slight modification of the interior mechanism of the burner. This may be seen by unscrewing the stem at the milled ring. In the center of the circle which forms the inner end of the stem, is an eighth-inch opening, and at the circumference is a pin-hole, both for admitting gas to the crown of the burner. When the parts (stem and crown) are in place, a quarter-inch disk faces the end of the stem, and is adjustable, in regard to its distance from the end, by means of the threaded shaft to which it is attached or, more accurately, of which it is a part. The shaft itself is shifted toward or from the end by the key underneath the crown. The motion toward the end at its limit brings the disk in contact with it, and more or less perfectly closes the larger opening; the pin-hole being beyond the circumference of the disk remains open.

This construction does not admit of the required perfect control of the gas-supply to the individual burner. The smallest quantity of gas that may enter produces generally too large a flame when little heat is needed, and the pin-hole prevents entirely cutting off the supply. This difficulty is resolved and the burner completely adapted to the present purpose by merely closing the pin-hole and placing a circular washer of soft leather, with a small segment removed, on the disk. If the crown and stem be now screwed together, the washer is compressed between the disk and the end of the stem, tightly closing the remaining opening in the latter. Unscrewing the parts but slightly, relieves the pressure and renews communication between the stem and the crown. The manner of manipulation with the burner thus modified is plain. Additional comment is unnecessary.

The pipe *G* is strapped to the flat bar supporting it, by strips of brass fastened with screws, and is therefore readily detached. The bar is attached to the legs of the stand in the manner described for those carrying the burners in Fig. 5, and is also adjustable as regards its level. Four spring-clamps projecting horizontally from the brass rail *R* hold the flasks securely in their places. The rail is screwed to the stand underneath the top frame. *R* further has two vertical clamps *J* similar to those just mentioned. They grasp the glass tube *H*, which is closed at one end by a rubber cap and connected at the other with a hydrogen-generator. Through *H* hydrogen is distributed to the flasks. For this purpose there is a short branch opposite each flask. The neck of the flask is closed by a rubber stopper, through which pass three glass tubes. One of these, *k*, is connected by rubber tubing with the branch to which attention was called, and reaches to the bottom of the flask. The lower end is drawn out and bent upwards slightly. By means of a compressor, the rubber tubing making the connection may be opened or closed as desired. The dropping-funnel *I*, for introducing the acid, has a wide-mouthed bulb large enough to contain the whole of the acid required for the solution; the stem holds a column of acid capable of more than overcoming the resistance offered by the solution in the cadmium chloride tubes, the ten by one-inch lipped test-tubes, *A*. The tube *E* with two bulbs conducts the gases generated in the flask into the cadmium solution in *A*. The test-tubes stand, in the rack *S*, upon a pad of sheet rubber.

Economy of space, the ease, nicety, and rapidity of manipulation possible with it, and the ability to use the device wherever the little space occupied by it may be found in the draft-chamber, are its practical features. Where a large number of determinations must be made at one time the number of stands may be correspondingly increased and controlled by one operator.

LABORATORY OF THE BLACK DIAMOND  
STEEL WORKS, PITTSBURG, PA.

[CONTRIBUTIONS FROM THE ANALYTICAL LABORATORIES OF COLUMBIA  
UNIVERSITY.]

## THE INSOLUBLE CARBOHYDRATES OF WHEAT.

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### PART I—DESCRIPTIVE.

#### A. WHEAT STARCH.

The constitution of wheat starch has been thoroughly investigated by L. Schulze.<sup>1</sup> A very carefully prepared air-dried starch was employed, allowance being made in the calculations for moisture present in the sample. His results, obtained both by

<sup>1</sup> *J. prakt. Chem.*, 136, 311.

elementary analysis and by estimation of the dextrose formed on hydrolysis, show conclusively that the formula of wheat starch is  $n(\text{C}_6\text{H}_{10}\text{O}_5)$  and not, as supposed by Naegeli,  $\text{C}_{48}\text{H}_{80}\text{O}_{42}$ .

The separation of starch from accompanying carbohydrates has been discussed in another paper<sup>1</sup> and will be referred to in speaking of analytical methods (page 302).

#### B. HEMICELLULOSE—PENTOSANS.

The term hemicellulose has been introduced by E. Schulze<sup>2</sup> to designate the carbohydrate matter yielded to boiling dilute acids by vegetable cells from which the starch has been removed. It is a portion of the cell-wall rather than of the cell contents.<sup>3</sup> The fact that the hemicellulose of wheat yields both arabinose and xylose on hydrolysis has already been noted.<sup>4</sup> In general, however, it must be said that the amount of substance which was obtained for identification was so small in proportion to that hydrolyzed as to suggest the question whether the result could be taken as proving the absence of other sugars. I decided to try a method which should not depend upon recrystallization.

*Preparation of Sample.*—Wheat bran<sup>5</sup> was extracted successively with water, saline solution, malt extract, two per cent. ammonia, cold two per cent., and boiling one-tenth per cent. sodium hydroxide. Each reagent was removed by thorough washing with water before the application of the succeeding one. This treatment removed, beside fatty and resinous matter, all of the soluble carbohydrates and starch and nearly all of the proteid matter without the use of any acid. The residue consists essentially of cell-walls.<sup>6</sup>

The residue from the extraction with ammonia contained, in the air-dried state, 8.30 per cent. moisture, 8.50 per cent. proteids (nitrogen  $\times 6.25$ ), and 3.69 per cent. ash. It yielded, on the basis of non-nitrogenous ash-free substance, 27.62 per cent. furfural (determined as described in Part II) equivalent to 50.82 per cent. pentosans.

<sup>1</sup> *School of Mines Quarterly*, 17, 356.

<sup>2</sup> *Ztschr. phys. Chem.*, 16, 387-391.

<sup>3</sup> Prof. C. Cramer, in connection with Schulze's work.

<sup>4</sup> Stone: *Ann. Chem. (Liebig)*, 249, 230; Steiger and Schulze: *Ber. d. chem. Ges.*, 23, 3110; E. Schulze: *Ztschr. phys. Chem.*, 16, 397.

<sup>5</sup> Bran was used instead of the whole grain because it contains all the insoluble carbohydrates of the latter and does not require the removal of so much starch.

<sup>6</sup> Cramer: *Loc. cit.*

The sodium hydroxide extract contained pentosans, giving the characteristic red coloration with phloroglucin in hydrochloric acid and yielding furfural when distilled with hydrochloric acid.

The air-dried residue contained 7.65 per cent. moisture, 1.25 per cent. proteids, and 3.31 per cent. ash. On the basis of non-nitrogenous, ash-free substance, it yielded 25.62 per cent. furfural equivalent to 48.13 per cent. pentosans.

*Hydrolysis of the Hemicellulose.*—As it was necessary to choose a somewhat arbitrary treatment, I adopted that which forms a part of the ordinary method of food analysis; *viz.*, thirty minutes boiling with 1.25 per cent. sulphuric acid. About one-half of the substance dissolved. The residue was washed free from acid and preserved for further examination.

To the solution sufficient sulphuric acid was added to bring the total present to two per cent., and it was then boiled gently with a reflux condenser until the reducing power of the solution no longer increased (six hours). This reducing power was found to be equivalent to 91.2 per cent. of that of dextrose and showed that the solids in solution consisted almost entirely of reducing sugars. A second determination showed the organic solids in solution to have a reducing power of 91.3 per cent. of that of dextrose.

*Qualitative Tests.*—The solution was tested<sup>1</sup> for mannose with phenylhydrazine acetate, for galactose by evaporation with nitric acid, and for levulose by resorcin in hydrochloric acid. All of these tests gave negative results. Reactions of the pentoses indicated their presence in larger proportion. No direct test for dextrose, applicable under these circumstances being known, the osazone was next prepared.

*Preparation of the Osazone.*—This was carried out essentially as described by Gans and Tollens.<sup>2</sup> A part of the solution was concentrated on the water-bath until it contained ten per cent. of solids, cooled to 70°, and then mixed with an equal volume of a solution containing for each gram of carbohydrate treated, two grams phenylhydrazine hydrochloride and three grams of sodium acetate. The mixture was kept at 65°–70° for about forty-five minutes and then allowed to cool. The osazone separated as a

<sup>1</sup> Lippmann: *Chemie der Zuckerarten*, 338, 395, and 483.

<sup>2</sup> *Ann. Chem.* (Liebig), 149, 249.

yellow iridescent precipitate which was collected, washed thoroughly and dried without recrystallization. Thus it was hoped to secure a product nearly representative of the entire solution, and whose composition should show the relative proportions of pentose and hexose present. As the yield of osazone is never quantitative, this method cannot be regarded as absolutely accurate, but, on the other hand, both dextrose and the pentoses form their osazones easily and freely under the conditions described.

Since Stone<sup>1</sup> has found that the osazones of the pentoses are soluble in about fifty parts of water on continued boiling, while glucosazone is quite insoluble, the proportion of the latter, if any were present, could be largely increased by dissolving away most of the pentose compound. Accordingly a part of the osazone described above was boiled for ten minutes with about forty parts water, whereby about three-fourths was dissolved. The residue was dried and analyzed as was the original preparation.

*Analysis of the Osazones.*—The percentage of nitrogen in each of the preparations was determined by Dumas' method with the following results :

*First Preparation.* — Original precipitate ; *a.* 0.1716 gram yielded 26.6 cc. nitrogen at 29.5° and 764.4 mm. pressure.

*b.* 0.1694 gram yielded 25.8 cc. nitrogen at 20.0° and 759.4 mm. pressure.

*Second Preparation.*—Residue ; 0.0993 gram yielded 14.8 cc. nitrogen at 21.0° and 761.0 mm. pressure.

From which we obtain :

	Nitrogen. per cent.	Nitrogen. per cent.
Original precipitate .....	$\left\{ \begin{array}{l} a. 16.98 \\ b. 17.16 \end{array} \right\}$	Average.. 17.07
Residue from boiling water.....		16.99
Calculated for $C_{17}H_{20}N_4O_8$ (from pentose).....		17.07
“ “ $C_{18}H_{22}N_4O_4$ (from hexose) .....		15.64

The hemicellulose of wheat appears then to yield on inversion only pentoses and, therefore, to consist of pentose anhydrides or true pentosans.

#### C. CHARACTERISTICS OF THE FIBER.

*Composition and Color Reactions.*—The residue from the action of sulphuric acid, after washing with water and alcohol and dry-

<sup>1</sup> *Am. Chem. J.*, 13, 662.

ing in the air, was of a medium brown color and loose fibrous texture. It contained 3.43 per cent. moisture, 0.65 per cent. ash, 0.25 per cent. nitrogen, and yielded 11.46 per cent. furfural. It showed well the deep magenta color (produced by lignin) when treated with chlorine and then boiled with sodium sulphite, and gave the red coloration when heated with the phloroglucin reagent (test for pentosans). No coloration was obtained on treating the fiber with a solution of fuchsin decolorized with sulphurous acid nor on boiling with anilin sulphate (tests for oxycellulose).

*Reactions with Ferric Chloride and Potassium Ferricyanide.*—Jute fiber, when immersed in a solution containing molecular proportions of the above reagents, fixes upon itself a large proportion of ferrous ferricyanide as a uniform deep-blue dye. This is considered by Cross and Bevan<sup>1</sup> as one of the most characteristic reactions of the lignocelluloses of which jute is the type.

In my experiments on the wheat fiber, I used a fresh mixture of equal volumes of aqueous solutions containing in 100 cc., one and six-tenths grams ferric chloride and three and three-tenths grams potassium ferricyanide respectively. The increase in weight of the fiber after immersion in this solution was determined by collecting in a Gooch crucible, washing well with cold water, and drying at 105°. The following quantitative experiments were made :

**SERIES A.—TIME VARIED. MASSES CONSTANT.**

Weight of fiber. Gram.	Volume of mixed solution. cc.	Time of immersion.	Increase in weight. Per cent.
1.00	20	20 min.	9.40
1.00	20	1 hour	11.17
1.00	20	10 hours	11.16

With these proportions, then, the reaction proceeds rapidly to the maximum.

**SERIES B.—TIME VARIED. MASSES CONSTANT.**

Weight of fiber. Gram.	Volume of mixed solution. cc.	Time of immersion. Hours.	Increase in weight. Per cent.
1.00	20	16	11.26
1.00	40	16	21.81
1.00	60	16	30.49
1.00	80	16	36.71
1.00	100	16	46.70

<sup>1</sup> Cellulose, p. 124-131.

Wheat fiber has, therefore, like the typical lignocellulose (jute), the power of fixing upon itself an amount of the cyanide varying roughly with the amount exposed to its action. This reaction is very interesting as showing the similarity of the lignocellulose molecule in these tissues. It will be shown to be of value also as a test of the purity of cellulose.

#### D. LIGNONE CHLORIDE.

Cross and Bevan<sup>1</sup> have isolated a compound from chlorinated jute fiber to which they give the above name. Its composition corresponds to the formula  $C_{11}H_{11}ClO_2$  and is constant after fractional precipitation and when prepared under varying circumstances. It is precipitated as yellow flocks when its alcoholic solution is diluted with water.

Seventy-five grams of the fiber already described was boiled with one per cent. sodium hydroxide, washed, pressed to remove most of the water, treated with chlorine gas for one hour, washed free from hydrochloric acid, and covered with alcohol. On pressing out the alcoholic solution it was found to be of a deep golden yellow color. On concentrating and pouring into water a part only of the dissolved substance separated, as was shown by the color of the supernatant liquid. The precipitate obtained, although small (about one-half gram), corresponded in appearance with that described and on collection and analysis showed 26.7 per cent. chlorine, or just the amount required by the above formula. This seems sufficient evidence of the identity of the products.

I do not know that this compound has previously been prepared from any other source than commercial fibers, but the fact that it may be obtained from such a widely different tissue as that of the coat of the wheat kernel would indicate that this type of lignification may be general among plants of annual growth.

On the other hand, the amount recovered is too small to justify much speculation until further results are obtained.

#### E. CELLULOSE.

For the separation of cellulose three very different methods were tried.

1. *F. Schulze's Method*.—Thirty grams of the fiber was treated

<sup>1</sup> Cellulose, p. 135.



at ordinary temperature with a solution of twenty-five grams potassium chlorate in 350 cc. of nitric acid (1.10 sp. gr.). After standing seven days with occasional stirring, the strength of nitric acid was raised to 1.13 sp. gr. by the addition of concentrated acid, and the digestion continued for another seven days. Finally, the mixture was kept at about 40° for two hours, then filtered, washed free from acid, and treated on the filter with cold two per cent. ammonia as long as the filtrate was colored, and the washing finished with water and alcohol.

The sample seemed particularly resistant to this treatment so far as appearance was concerned. Instead of becoming white, it attained during the first two or three days a dull flesh color which was not materially changed during the remainder of the fortnight. The color of the dried residue was light brown, very much lighter than, but still suggesting, that of the original fiber. By repeating the treatment or increasing its severity a purer residue could doubtless be obtained but, as the yield is already less than that from the method next to be described, there seems no object in experimenting in this direction.

The residue constituted 66.0 per cent. of the original. It yielded 7.00 per cent. furfural and gave the red coloration when heated with phloroglucin. When boiled with anilin chloride it was tinged very faintly reddish, indicating a trace of oxycellulose. From twenty parts of the standard cyanide solution it absorbed 6.04 per cent. of its weight of the pigment, indicating, as comparison with the other cellulose will show, that the lignin group was not selectively attacked.

2. *Method of Cross and Bevan.*—Thirty grams fiber was boiled thirty minutes with 800 cc. of one per cent. sodium hydroxide, filtered, washed with water till free from alkali, squeezed as free from the water as possible, and then exposed in this moist condition to the action of chlorine gas in a covered beaker at ordinary temperature for one hour with occasional stirring. The color changed rapidly from brown to light lemon-yellow. At the end of the hour it was brought upon a filter and washed with water till free acid was removed, then heated to boiling with 600 cc. of two per cent. sodium sulphite and sufficient sodium hydroxide solution added to make two-tenths per cent. of the whole. The boiling was continued five minutes, the solu-

tion filtered hot and the residue washed until the washings were neutral and colorless. It is convenient to use a muslin filter and hasten the operation by squeezing out the washings. Finally the washing was finished with alcohol and the residue dried and weighed.

This process yielded 66.5 per cent. of residue of a light creamy color and free from nitrogen. It yielded 5.62 per cent. of furfural and gave a distinct coloration with phloroglucin, but not with anilin chloride. From the cyanide solution it absorbed only 0.92 per cent.

3. *Lange's Method of Fusion with Alkali*.—Bring five to ten grams of the (fat-free) substance into a porcelain crucible about three inches high with three times as much caustic potash and about twenty cc. of water. Heat with stirring in an oil-bath not above  $180^{\circ}$ , keep at this temperature ( $175^{\circ}$ – $180^{\circ}$ ) for an hour, cool to  $75^{\circ}$ – $80^{\circ}$ , add about seventy-five cc. hot water, cool, acidulate with sulphuric acid, make slightly alkaline with sodium hydroxide, and separate the precipitate by means of a centrifugal machine. The liquid is poured off and the cellulose washed with hot water, separating in the same way. Bring onto a filter; wash with water, alcohol and ether, dry and weigh. Incinerate and deduct the ash.<sup>1</sup>

Ten grams were used for each determination; the melting proceeded quietly and without troublesome frothing. The precipitate was allowed to settle by standing instead of separating by centrifugal force. Thus obtained it was of a somewhat slimy character, and the process of filtering and washing is therefore slow. This is the only difficulty of manipulation which the method presents. The cellulose dried to a white powder, the fibrous nature having been destroyed by the treatment.

Lange obtained higher results by this method than by that of Schulze, but in this case I recovered only 39.3 to 43.1 per cent. cellulose (without allowing for ash). The product yielded 3.96 per cent. furfural and gave the phloroglucin reaction, although not so markedly as did the other preparations of cellulose. Boiled with a solution of anilin salt it showed no evidence of any oxycellulose. From the cyanide solution it absorbed 0.89 per cent.

<sup>1</sup> *Anal. angr. Chem.*, 1885, 561.

*Choice of Method of Preparation.*—For reasons which are mainly obvious, but which will be reviewed in speaking of analytical methods, the process of separation by means of chlorination is preferred, and cellulose thus obtained was employed in the following experiments.

*Action of Strong Sulphuric Acid.*—Strong sulphuric acid (100 parts sulphuric acid and seventeen parts water) dissolves pure cotton cellulose with only very slight coloration and the solution when diluted and boiled yields dextrose. E. Schulze<sup>1</sup> has found the same to take place with cellulose residues from other natural tissues prepared by vigorous acid hydrolysis followed by F. Schulze's reagent, although the amounts of dextrose obtained were small.

When applied to the cellulose described above, under the conditions given by Schulze, the solution was not complete and a very considerable discoloration was produced. The undissolved portion (nearly one-fifth) did not yield a measureable amount of furfural. The final product of hydrolysis of ten grams of the cellulose, converted into osazone in the usual way, gave only 1.31 grams of the latter. Its composition is shown by the following results:

*a.* 0.1914 gram gave 25.9 cc. nitrogen at 23.8° and 775.5 mm. pressure, equal to 15.48 per cent. ; *b.* 0.1870 gram gave 24.7 cc. nitrogen at 17.0° and 771.0 mm. pressure, equal to 15.58 per cent. ; average 15.53 per cent. ; calculated for  $C_{12}H_{22}N_4O_4$  15.64 per cent.

The osazone is, therefore, that of dextrose and the specific products of hydrolysis of the furfural-yielding group do not appear.

*Action of Cold Dilute Sodium Hydroxide.*—Twenty grams cellulose was treated with 400 cc. five per cent. sodium hydroxide at room temperature with occasional stirring for two days, filtered and washed. The filtrate was light brown in color, and on neutralizing with hydrochloric acid a white precipitate was formed. I was not able to separate this precipitate quantitatively, but enough was collected to show its general resemblance to wood gum, and it gave the characteristic deep red coloration with phloroglucin. The residue constituted about eighty per

<sup>1</sup> *Ztschr. phys. Chem.*, 16, 414.

cent. of the amount treated. It was whiter than before treatment. A determination of furfural gave 3.34 per cent., equal to 2.67 per cent. of the original. Hence less than one-third of the dissolved substance was pentosan, and the suggestion of Hoffmeister<sup>1</sup> that this treatment be inserted as a step in the determination of cellulose, would seem of no value.

*Chemical Nature of the Cellulose.*—The term cellulose is here used in an inclusive sense to designate the strictly carbohydrate radicle as opposed to the more or less "condensed" lignin substance with which it is combined in the lignocellulose. The abnormal characteristics of this sample (property of yielding furfural and coloring phoroglucin reagent) I believe to be due to the inherent nature of the cellulose itself rather than to imperfect methods for its separation, except in the case of Schulze's method. The sample contains about ten per cent. of penta-anhydride which appears to be chemically combined with a part at least of the hexa-anhydrides (normal cellulose). It may be well now to review some of the reasons for this belief.

1. The absence of lignin groups is strongly indicated (*a*) by the fact that the repetition of the chlorination followed by treatment with sodium sulphite gave no red coloration, and very slight loss of weight, (*b*) the insignificant amount of cyanide absorbed (less than one per cent.)

2. The method of fusion with alkali, totally different in its nature, causing complete disintegration of the fiber and a much lower yield than the chlorination method, still produces a cellulose in which the abnormal characters differ only in degree from those shown by the product of the latter process.

3. The imperfect solubility in sulphuric acid and the small amount of glucosazone formed from the product of hydrolysis indicate that the cellulose is not of the normal type.

4. The proportions of substances extracted by dilute alkali show that the sample is not a simple mixture of pentosan and normal cellulose.

5. Somewhat similar characters have been found by others<sup>2</sup> in studying natural celluloses prepared by other methods than

<sup>1</sup> Landw. Versuch-sta., 39, 461.

<sup>2</sup> C. Schulze and Tollens: Landw. Versuch-sta., 40, 367; Hoffmeister: Landw. Versuch-sta., 39, 461; Winterstein: Ztschr. phys. Chem., 17, 391; E. Schulze: Ztschr. phys. Chem., 16, 414.

those (Cross's and Lange's methods) to whose products the above statements refer.

#### F. FURFURAL-YIELDING CONSTITUENTS.

Some of the facts observed in connection with this class of bodies would seem worthy of mention here. They constitute nearly or quite one-half of the seed-coat exclusive of starch and proteids—a much higher proportion than is found in woods, straws, or commercial fibers—and by far the greater part is in the form of easily hydrolyzed pentosans. The physical effect of these in rendering the tissue more tenacious and more retentive of moisture is doubtless of considerable physiological significance. It was observed in the course of this work that the samples which had not been treated with acid held about twice as much hygroscopic moisture as did those from which the pentosans had been removed, when similarly air-dried. In the case of isolated xylan, this affinity for moisture is so great as to be a most serious obstacle to its analysis.<sup>1</sup>

The wide distribution of furfural-yielding bodies among the different chemical groups which compose the cell-wall has been shown by the quantitative determinations mentioned above, in the original tissue, in the fiber remaining from acid treatment, in the cellulose isolated from the latter by various methods, and in cellulose which had been further treated with dilute sodium hydroxide. We have also seen that all of these specimens gave distinct pentosan reactions<sup>2</sup> with phloroglucin and that none of them gave distinct oxycellulose reactions with anilin salts. We therefore conclude that the furfural-yielding constituents of wheat are essentially pentosans in some form and that we commit no serious error in interpreting the amount of furfural obtained as a measure of the total pentosans present. But if we should use the term *pentosans* in this exclusive sense and stop here, it would be little more satisfactory than to include dextrin, starch, and cellulose in one group of *hexosans*. Our pentosans would con-

<sup>1</sup> Johnson: This Journal, 18, 214.

<sup>2</sup> NOTE.—While the work was in progress the results of Cross and Bevan on the furfurals of straws appeared (*J. Chem. Soc.*, 69, 804-818). In view of the purple reactions with phloroglucin found by them, it was thought best to retest all the celluloses side by side with a pentose solution. Especially in the cases where the reaction was least marked, the color appeared somewhat darker and not so clear as in the pentose solution, but the difference seems to be due to the degree of heat used to develop the color. When the phloroglucin compound was precipitated by boiling and then dissolved in alcohol, no such differences were found in the alcoholic solutions.

stitute practically all of the hemicellulose, about forty per cent. of the lignin group or non-cellulose of the fiber, and about ten per cent. of the cellulose (chlorination method). It would seem much better, therefore, to distinguish between those pentosans which are easily dissolved by dilute acids without materially affecting the cellulose or lignin, and those which on the other hand, are resistant to acid, or to both acid and alkaline, hydrolysis. The former are evidently not combined with hexose groups and they may be considered as true or free pentosans; the latter are apparently in chemical combination, partly in the lignin group and partly in the cellulose.

## PART II—ANALYTICAL.

### A. SEPARATION OF THE INSOLUBLE CARBOHYDRATES.

It is customary in cereal analysis either to be content with the results of the Weende method or to determine in addition the starch and perhaps also the furfural obtainable and calculate the latter to pentosan. The latter determination we have seen to be to a certain extent misleading since a part of the furfural comes from bodies in combination both in the cellulose and in the lignin groups and while apparently of a pentose nature, these are quite different in their properties from the true pentosans of the hemicellulose. In order to separate quantitatively the carbohydrates described in the first part of this paper, it is necessary to combine the methods best adapted to the determination of each into a single scheme. So much time was required to test the different methods and the products yielded by them that some of the details are in need of further study and the results are offered as approximate rather than absolute or final. An outline of the scheme is given and is followed by a discussion of the different steps. An application of the scheme is found in Part III.

1. *Determination of Starch.*—The results of a comparison of several methods on a series of samples specially selected to show gradations in the amount of starch present, has been published in the *School of Mines Quarterly*,<sup>1</sup> and abstracted in the *Analyst* for January, 1897. These results show the superiority of the malt extract method and the safety of completing the inversion of the solutions with hydrochloric acid by boiling as suggested by Hibbard,<sup>2</sup> instead of by long heating on the water-bath.

<sup>1</sup> Vol. xvii, No. 4.

This Journal, 17, 64.

SCHEME OF ANALYSIS USED.<sup>1</sup>

Five grams of the sample (previously extracted with ether) are stirred with about 100 cc. water for a few minutes, filtered, and washed.				
Soluble carbohydrates as dextrin.	Starch.	Free pentosans.	Lignin and allied substances.	Cellulose.
Filtrate.—Add one-tenth its volume of 25 per cent. HCl and heat with a reflux condenser for two and one-half hours on a water-bath, or boil thirty minutes on a sand-bath.  Clarify, if necessary, and determine the dextrose present in an aliquot portion, by means of Fehling's solution, and calculate to	Residue.—Wash into a beaker with about 100 cc. water (more if the proportion of starch is high), heat to boiling, cool partially, and invert with malt extract till starch disappears, filter, and wash.  Filtrate.—Treat as in the case of the preceding filtrate and calculate the dextrose found to	Residue.—Boil thirty minutes with 1.25 per cent. H <sub>2</sub> SO <sub>4</sub> , filter, and wash with water and alcohol.  Filtrate.—Add sufficient H <sub>2</sub> SO <sub>4</sub> to make 2 per cent. Boil gently with reflux condenser for six hours. Determine reducing power; calculate to pentose and thence to	Residue.—Dry and weigh. In a duplicate residue, determine proteid (and ash) and correct the weight accordingly.  Treat according to the method of Cross and Bevan, dry, and weigh the residue.	Residue, less proteid if present (and ash), equals

<sup>1</sup> Since this work was finished, a method for the determination of carbohydrates in cereals, devised by Prof. W. R. Stone, has been published by the U. S. Department of Agriculture (Bul. 34, Office of Experiment Stations). See also this Journal for March, 1897. Stone will be found in this issue.

2. *The Determination of True Pentosans.*—Reference has been made to the interpretation of furfural as a measure of pentosans (p. 302). It has been shown that by hydrolysis of the hemicellulose solution, pentoses only are obtained. Since, moreover, isolated pentosans are readily dissolved by dilute acids, it is evident that hydrolysis of this solution and determination of the pentosans formed must give a fairly accurate measure of the true pentosans. The kind and strength of acid used should be a subject for further study. Sulphuric acid was used in this work because the pentoses are so little altered by long boiling with it.<sup>1</sup> The reducing power was referred to dextrose by Allihn's table and the pentose taken as ninety-seven per cent.<sup>2</sup> of the amount of dextrose indicated.  $\text{Pentose} \times 0.88 = \text{pentosan}$ .

3. *The Determination of Cellulose.*—The three methods compared have been described above (pp. 296, 297, 298). Exposing to chlorine after simple wetting without alkaline treatment, and then proceeding as in the chlorination method has been tried and the results are tabulated with those obtained by the regular methods. The fiber itself is also shown for purposes of comparison.

Method.	Description of Product.				Color.
	Yield per cent.	Furfural per cent.	Nitrogen per cent.	Ferricyanide fixed; per cent.	
Cross and Bevan . . . . .	66.5	5.62	0.00	0.92	Light cream.
Lange . . . . .	41.2	3.96	0.03	0.89	Nearly white.
Schulze . . . . .	66.0	7.00	0.22 <sup>3</sup>	6.04	Light brown.
Chlorination alone . . . . .	84.3	8.89	0.08	2.02	Very light brown.
Original sample . . . . .	100.0	11.46	0.25	11.17	Brown.

It is evident that no one feature can be urged as a criterion in judging between the methods but all must be taken into consideration. Such a comparison shows the superiority of the chlorination method. It also suggests the possibility of increasing the yield without detriment to the quality of the product, by making the preceding alkali treatment less severe.

The reaction with the ferricyanide solution (p. 295) seems of considerable value in testing the purity of celluloses. When the sample increases only slightly (about one per cent. or less) in

<sup>1</sup> Tollens and Schulze: *Landw. Versuch-sta.*, 40, 379-384.

<sup>2</sup> Stone: *Am. Chem. J.*, 13, 73.

<sup>3</sup> Exclusive of 0.07 per cent. ammoniacal nitrogen (from the wash solution) determined by distillation with magnesia.



weight and is dyed only a bluish-green instead of a deep blue color, it is at least a very strong indication that lignin substances are not present in notable quantity. When the original fiber is dark-colored, the appearance of the cellulose will also serve as a guide, for unless this color has disappeared, it is probable that the lignin group has not been completely removed.

The significance of the furfural-yielding property of these celluloses has been discussed in the first part of this paper.

4. *Lignin and Allied Substances*.—These are determined by loss of weight when cellulose is isolated from the fiber. The general characteristic feature of the substances is their susceptibility to alkali. This is the principle upon which Lange's method is based; but since the treatment called for by the latter evidently attacks the cellulose, it is best to remove the more readily soluble portion by boiling with dilute alkali and then treat with chlorine to convert the remainder into a more easily soluble compound. The first step is also introduced in the current analytical methods, and the term lignin is usually restricted to the portion which remains with the cellulose in the "crude fiber." There is, however, no established chemical difference on which to rest such a distinction, and it is, therefore, omitted here, although the step might easily be introduced if desired.

#### B. DETERMINATION OF COPPER REDUCTION.

Wherever in this paper, the reducing power of a solution is given, the determination has been made by adding twenty-five cc. of the solution to be tested to an excess of boiling Fehling's solution under the usual conditions of dilution, boiling exactly two minutes, collecting and estimating the cuprous oxide and taking the corresponding value for dextrose from Allihn's table. In most cases the cuprous oxide was determined as follows:<sup>1</sup> Collect the reduced oxide on asbestos in a filtering tube and wash well with water. Dissolve on the filter with nitric acid and wash thoroughly into a flask. To the solution add excess of sodium carbonate and dissolve the precipitate with one cc. of ammonia (0.96 sp. gr.). Titrate with a recently standardized solution of potassium cyanide until the color disappears.

The method is rapid and accurate since no other heavy metals than copper can be present. Before adopting it I checked it

<sup>1</sup> Lavenne: *School of Mines Quarterly*, 17. No. 4.

against the electrolytic method and made a large number of experiments to show that varying amounts of sodium nitrate had no effect upon the result. After a little practice in determining the end reaction, I believe the results obtained should be as accurate as by the gravimetric methods, and much more accurate than simple titration with Fehling's solution.

#### C. DETERMINATION OF FURFURAL.

The method used was essentially that of the Association of Official Agricultural Chemists, but as that may not be available to all, and as some of the details were modified, it is given in full.

From two to five grams of the sample are placed in a flask with 100 cc. of hydrochloric acid of 1.06 specific gravity. The mixture is distilled and the distillate collected in a graduated receiver. Each thirty cc. lost by distillation (which should require from ten to fifteen minutes), is replaced by thirty cc. of hydrochloric acid of the strength mentioned above. Continue the process until a drop of the distillate produces no red coloration in a slip of filter paper moistened with anilin acetate. Eight to twelve distillations are usually required. Add to the distillate sufficient water to bring to a volume of 400 cc. and for every fifty cc. of water added, add 10.2 grams sodium chloride. Neutralize exactly with sodium carbonate, and add ten cc. of a solution of phenylhydrazine acetate, made by mixing twelve grams phenylhydrazine with seven and five-tenths grams glacial acetic acid and diluting to 100 cc. Stir thirty minutes and let stand in a dark closet until the following day. Filter on glass wool in glass filtering tubes six to seven inches long, removing the precipitate which adheres to the beaker by means of a feather. Dry to constant weight in an air-bath at 55° to 60° in a slow current of dry air. A partial vacuum is produced in the tube by means of suction, the supply of air being regulated by stop-cocks. Finally the precipitate is dissolved by hot alcohol, the tube dried and weighed and the loss of weight calculated as furfural hydrazone. For reducing to furfural and to pentosans the following formulas were used :

$$\begin{array}{lcl} \text{Hydrazone} \times 0.516 + 0.0104 & = & \text{furfural,} \\ \text{Furfural} \times 1.84 & & = \text{pentosans,} \end{array}$$

the factor for pentosans is obtained by averaging those of xylan and araban.

The following results obtained after only a very few preliminary trials, show what agreement may be expected without much practice.

Sample.	Weight taken. Grams.	Hydrazone obtained. Grams.	Furfural. Per cent.
A .....	3.860	0.836	11.46
	3.860	0.829	11.36
	3.860	0.845	11.57
B .....	3.870	0.393	5.54
	3.870	0.404	5.70
C .....	3.670	0.559	8.14
	3.670	0.561	8.17
	3.670	0.551	8.03
D .....	3.628	0.314	4.78
	3.628	0.311	4.74

### PART III. PHYSIOLOGICAL.

#### INTRODUCTORY.

In questions of nutrition the proportion of food and of each of its proximate ingredients which is digested, *i. e.*, which leaves the alimentary canal and enters the physiological interior of the body, is evidently the basis of all further studies. While the different substances digested are not all utilized to the same extent, and while the undigested residue undoubtedly performs an important physiological function, these facts only serve to show the necessity of further study based upon the "digestive coefficients" and do not detract from the value of the latter when properly interpreted. Such digestive coefficients to be comparable must of course be determined by uniform methods. The analytical method used by the experiment stations in this country is published by the U. S. Department of Agriculture.<sup>1</sup> The work of these stations, as well as important foreign work, is periodically reviewed in the Experiment Station Record.<sup>2</sup> A yearly digest of the subject is included in the *Jahresbericht für Agricultur-chemie*, and it has been treated by Dietrich and König.<sup>3</sup>

It is mainly upon these experiments with animals that we are obliged to base our estimates of the digestibility of wheat and wheat products since the published results of experiments with

<sup>1</sup> Bul. 46, Division of Chemistry.

<sup>2</sup> Published by the U. S. Department of Agriculture.

<sup>3</sup> Zusammensetzung und Verandlichkeit der Futtermittel.

men<sup>1</sup> are very incomplete. But the results obtained by current methods of analysis give little information regarding the carbohydrates, this group being simply divided by an arbitrary line (sometimes considered a rough imitation of the digestive process, into "nitrogen-free extract" and "crude fiber."

Recently a number of determinations of digestibilities of total furfural-yielding substance have been reported, especially by Stone<sup>2</sup> and Lindsey.<sup>3</sup> Those of wheat bran fed to different animals (sheep and rabbits) and at different times vary from fifty-nine to sixty-four per cent.

#### DIGESTION EXPERIMENT.

Having studied the chemical nature of the principal carbohydrates of wheat it is interesting to find the digestibility of each as determined by an actual experiment. I was fortunate in obtaining, through the kindness of Mr. H. J. Patterson, of the Maryland Experiment Station, samples of the food and feces from an experiment conducted by him<sup>4</sup> upon a steer fed with wheat bran only. The total dry matter digested was 68.33 per cent. of the whole. The samples were analyzed by the method outlined above, the small amount of ash in the cellulose being neglected. The results, calculated to the dry basis, are as follows:

	Food. Per cent.	Feces. Per cent.	Per cent. Digested.
Soluble carbohydrates as dextrin	7.2	0.7	96.9
Starch .....	17.7	0.0	100.0
Free pentosans.....	17.5	18.7	66.2
Cellulose .....	8.5	20.2	24.8
Lignin and allied substances ....	11.6	23.2	36.7
Protein <sup>5</sup> .....	20.49	11.04	82.96
Ether extract <sup>5</sup> .....	6.92	12.52	42.73
Ash <sup>5</sup> .....	6.05	11.04	42.21
Undetermined .....	4.04	2.60	...
<hr/>			
Nitrogen-free extract <sup>5</sup> .....	55.59	41.93	76.08
Crude fiber <sup>5</sup> .....	10.96	23.47	32.21

We see from the above that the digestibilities of the insoluble

<sup>1</sup> Compiled by Atwater: Bul. 21, Office of Experiment Stations, U. S. Department of Agriculture.

<sup>2</sup> *Am. Chem. J.*, 14, 9; *Agr. Sci.*, 5, 6.

<sup>3</sup> Mass. Station Report for 1894, p. 185-186.

<sup>4</sup> Maryland Station, Bul. 41, pp. 137-138.

<sup>5</sup> From Patterson's analysis.

carbohydrates range from 25 to 100 per cent. The "nitrogen-free extract" with a mean digestibility of seventy-six per cent. is composed of substances whose percentage digestibilities vary from 100 to less than forty. Even in the case of the crude fiber the digestibility of one of the constituents considerably exceeds that of the other. It must be borne in mind in this connection that the group of lignin and similar substances is divided by the current methods, part being included in the nitrogen-free extract and part in the crude fiber.

#### DIGESTIBILITY AND PHYSIOLOGICAL VALUE.

The final utilization of the normal carbohydrates absorbed by the healthy animal body is known to be practically complete. With lignin and pentosans or pentoses, the case seems to be different. It is held<sup>1</sup> that the lignin of vegetable tissues supplies directly the benzol radicle of the hippuric acid of the urine of herbivorous animals and is, therefore, but little oxidized in the body.

In the case of pentoses and pentosans whose identification is easy, the experimental methods are more direct, yet the results are very conflicting.

Ebstein<sup>2</sup> found that either arabinose or xylose given to men in doses of twenty-five grams, quickly appeared in the urine unchanged, and he concluded that these sugars were without nutritive value, or at least nearly so. This result has been largely quoted and its importance perhaps overestimated. Salkowski,<sup>3</sup> and Cramer,<sup>4</sup> in numerous independent experiments upon men, rabbits, and fowls, found that these sugars were mainly utilized, only about one-fifth (according to Salkowski) being given off in the urine. In many cases (according to Cramer) it was shown by killing the animals that the feeding of pentoses had caused an increased storage of glycogen in the liver. Finally Fretzel,<sup>5</sup> experimenting upon rabbits with xylose, has concluded that this sugar does not tend, either directly or indirectly, to promote the storage of glycogen.

<sup>1</sup> Meissner and Shepard: Untersuchungen über das Entstehen der Hippursäure im thierischen Organismus. Hanover, 1866. Stutzer: *Ber. d. chem. Ges.*, 8, 575. Weiske: *Zeit. Biol.*, 12, 24.

<sup>2</sup> *Archiv. pathol. Anat.*, 129, 401; *Centrbl. med. Wissens.*, 1892, 577.

<sup>3</sup> *Centrbl. med. Wissens.*, 1893, 193.

<sup>4</sup> *Ztschr. Biol.*, 19, 484.

<sup>5</sup> *Archiv. ges. Physiol.*, 56, 273.

The advisability of distinguishing between starch and pentosans in food analyses is thus emphasized not only by the difference in their digestibility but also by the possible difference in physiological value of the digested portions.

#### CONCLUSION.

The results obtained have been discussed under the different sections. It is unnecessary to repeat them here. I would, however, offer a final word of explanation in regard to the liberty taken with the words "cellulose" and "lignin substance." These are used to designate respectively the carbohydrate, and the more or less "condensed" portions of the fiber. That either is chemically homogeneous is certainly not claimed. It is with considerable hesitation that this work is presented at this time. The amount of undetermined matter is still larger than we should wish, but those who are interested in the subject will be familiar with its difficulties, and the separations which have been made may suggest some improvement on the ordinary "nitrogen-free extract" and "crude fiber" of cereal analyses.

#### DISCUSSION.

*Dr. Wiley:* Mr. President and Gentlemen, I think the paper is one of the greatest practical, as well as theoretical, interest. As one who has been engaged for a long time in the analysis of food products, I think it is a mark of great progress to know that we are getting finally to some definite knowledge of that large class of matters which, because it was not extracted, has always been called extract. It has been rather a matter of humiliation, I think, to agricultural chemists for many years that this term has been used in the way it has been. To designate a large part of cattle and human food as nitrogen-free extract is simply to do as doctors do when they say you are suffering from malaria or grippe. It is simply using words which have not much signification, to cover up a great deal of ignorance. It is gratifying that we are now making progress in this particular line. The work in this country which has been conducted by Mr. Sherman and others, and in England by Cross and Bevan, and in Germany by Tollens and his pupils, has all been in the direction of giving us more light on these bodies. The discovery of the five-atom sugars in cattle foods, and the methods of approximately

determining them was a great step forward, and the approximate determinations of lignin and cellulose or hemi-cellulose is another step. I think Mr. Sherman should congratulate himself, rather than feel sorry for the fact that he has finally reached a point where all but three or four per cent. of a sample can be distinguished and determined. It may not be that we have yet applied the right names to these bodies. The substances may vary a little from what they seem to be, but evidently they are composed of bodies which can be separated, and their digestibility can be determined. I think we are all, perhaps, struck with the statement given here of the low digestibility of the ether extract. Here is a substance which is just as important, except in the amount of it, as the other constituents of wheat. We have been for years bringing together under the term of ether extract, a large class of bodies which were generally supposed to be fats, but we all know the digestibility of fats is much higher than the coefficient mentioned in the paper. And this leads me to say what has long been known, that the ether extracts contain a great deal besides fats, and especially are likely to be mixed with chlorophyl, or its alteration products. These products doubtless will soon be the subject also of investigation, so that we may be able to separate the so-called ether extracts into true fats and into other bodies which are much less digestible. Still we should not, I think, be misled by digestibility. Because a body disappears during its passage through the intestinal canal, is no positive proof of its assimilation. Starch, as you see, disappears almost completely, during its transit through the assimilated canal, but that is no positive proof that starch is absolutely eliminated, any more than some of the other foods, less easily changed than starch. This change begins in the mouth during mastication in the alkaline action of the saliva and is continued in a large extent in the stomach before the acidity of the stomach becomes too great. It is supposed that after the ingestion of food through the esophagus the contents of the stomach remain alkaline for some time, and the conversion of the starch goes forward with great rapidity, and is continued, perhaps, after the acidity of the stomach has been established. The digestive coefficients have value in estimating the nutritive value of food. But we do not want food that is all



digested. If we were all put on a diet that is all digested, we would all die, because it is necessary for the purpose of digestion that the peristaltic action of the bowels be secured, and there must be something to excite this action. If you digest everything you eat you will derange the health and thwart the very purposes for which feeding is practiced. And hence these undigested bodies have a value, you may call it a negative value if you will, simply because they are not absorbed. Nevertheless, they have their uses in the animal economy. So the fact that a certain food product has a digestive coefficient of 100, another of 80, another of 60, another of 30, does not furnish sufficient data on which to base any correct idea of the actual value of those foods to the animal economy. They all have a value, not only a nutritive value, but a mechanical value, and this must not be lost sight of. In fact, the methods which we practice of valuing foods is faulty, whether we consider it from the view of the physiologist simply by the amount of it which is digested, or whether we consider it from the point of view of the chemist by the amount of heat which a food will give, or whether we view it simply from the light of the physician in regard to its general effect upon the system. That is, judging a food by any one of these three standards, we reach a false conclusion. They must all be combined in order to determine the true value of the food. In determining the value of these wheat carbohydrates as foods, we must look at them from the amount of heat that they will give, that is one of the functions of food; we must look at them from their coefficients of digestibility; and we must look at them, on the other hand, from the physician's or the hygienic point of view, from their effect upon the health. Now, if in valuing food we will keep these three points in mind, we will come to a very much better conclusion than if we insist upon judging it from a single standard. We know how apt we are to think that the particular thing we are doing is the only thing in the world which is worth doing, and that everybody must come to our standard of judging any particular thing, especially a food; but this is an erroneous idea.

From the analytical point of view, too, this paper is valuable. We are now beginning to reach a point where we can discriminate among these carbohydrates, not only in a qualitative, but



also in a quantitative way. For many years the methods of so simple a determination as that of starch were very much mixed up, and in fact, it is rather difficult, even to-day, to estimate the actual quantity of starch which is present in a cereal with absolute accuracy. Of course, I do not mean with approximate accuracy. The old methods of digesting a cereal with an acid and then determining the sugar, we know to be very faulty, but the modern methods of separating the starch are, as indicated by the speaker, approximately correct. The solution of starch by diastase is one of the methods very largely practiced in our own laboratory. We also aid the solution by heating in an autoclave to a high temperature. We think we get a little better results this way than by the use of the malt extract alone. The specific rotatory power of soluble starch gives another basis for the determination, and a rapid determination of the starch present, but the method has not proved satisfactory in our laboratory. After the starch is dissolved, then we can apply the acid and convert it into dextrose. By some one of these methods the starch can be separated, practically, from the other carbohydrates present in cereal grains. When we reach the bran we are at the very beginning of the word furfural, which, I believe, is derived from the Latin words which mean "bran oil." The fact of the derivation of this substance from the wheat bran has been known for many years. For fifty or sixty years, perhaps, the fact has been known that wheat bran would yield furfural when digested with an acid, although it was not known at the time that furfural was the splitting-up product of a five-atom sugar former. That was a matter of later knowledge. This substance is an old one, and yet it comes to us now under new forms and in new lights. The most difficult part of the problem, as indicated by the speaker, was the final separation of the lignins and cellulose, and allied bodies, and perhaps there is a great deal to be done yet before we reach final results. These bodies are so near each other and run into each other by such almost imperceptible gradations that it requires the highest degree of analytical skill, as well as of chemical research and investigation, to devise means by which they can be practically separated from one another. Therefore I think this Society should welcome all investigations of this nature, and I hope it

will not be long before this paper appears in full in the columns of the Journal.

*Mr. M. L. Griffin:* Mr. President and gentlemen, I have been very much interested in this paper presented this morning. It is in line with work which I have been connected with for some time, and as Mr. Stone and Dr. Wiley have said, any information on this subject is of great utility to this Society, to chemists, and to the chemical world. The difficulties of separating the bodies which have been referred to, are extreme, and any information, though incomplete, is certainly welcome.

We digest 110 cords of wood daily for paper-making at Mechanicville, N. Y., which illustrates how intimately the subject of this paper connects itself to the commercial world, not only in the digestion of carbohydrates by the animal economy but also to manufacturing industries. I venture to say that the commercial practice of separating cellulose from the intercellular and incrustating matter of wood or carbohydrates generally is very much ahead of the science of the subject.

The difficulty of making a laboratory separation of the components of wood or any carbohydrate resulting from plant growth lies in the fact that the more highly organized or developed molecules are a growth by continuous processes. If you will picture to your minds the growth of a tree from the coursing of the life-giving sap just under the bark where the latest growth is taking place to the heart of the tree, you will find a continuous development or growth with no clean cut gradations. This is the reason why it is so difficult to make definite separations within narrow limits.

Reagents which will dissolve incrusting and intercellular substances in wood are not without effect upon the cellulose itself.

This brings us to the methods laid down in books for the determination of cellulose in woody tissues. In brief they are summed up in alternate treatment of the samples over the water-bath, with an alkali and an oxidizing agent as chlorine or bromine. This is repeated until you get "pure cellulose."

You who have tried this, know how tedious it is and how worthless the results are, simply for the reasons given above. As technical chemists we know that a practical test for the

determination of cellulose in woody tissues by using small digesters in which we may subject the material to high temperature and pressure with suitable chemicals for a short time, will make a much clearer separation of cellulose and with less destructive effect. This is the method I employ for technical purposes.

We also know that some chemicals are more destructive to the cellulose than others in this connection. A chemical treatment in which the materials are not allowed to oxidize during the process of digestion, has a much less destructive effect on the cellulose, and produces a much more durable fiber for paper-making. The importance of this increased "yield", as manufacturers call it, is very apparent. The completeness of the separation of the cellulose from all foreign matter is equally important and desirable from every point of view.

I trust I have said nothing which will deter any chemist from undertaking work along this line. Our knowledge of the insoluble carbohydrates is very limited, and while we may only approximate the results we desire, there is a vast field here for highly valuable and useful service.

We may congratulate ourselves on the presentation of this paper by one of our members.

*President Dudley* : I would like to ask Mr. Sherman if the coefficient of digestibility of the whole wheat can be obtained from this paper ?

*Mr. Sherman* : No, it was just an experiment on the bran. The digestibility of the whole sample was 68.33 per cent. In regard to Mr. Griffin's remarks on the analytical methods, and especially for cellulose, I think that we will have to design our methods largely, at least as yet, according to the object we have in view. As I indicated, I do not think that we can say that cellulose, the cellulose we get from any given fiber, will be  $C_6H_{10}O_5$ , and nothing else ; in fact I am quite sure we cannot say that. What I have attempted was the separation on chemical lines, as far as possible, and as I am very free to admit, I did not get any pure cellulose ( $C_6H_{10}O_5$ ) by any of the methods, and the methods that gave the purest cellulose gave too low a yield. I think the chlorine method is much the best, because it attacks the lignin group selectively, and does not disintegrate the whole as the strong alkali usually does. This cellulose

consists of both hexose anhydrides and pentose anhydrides; I am not prepared to say whether that would be suitable for paper-making or not; I should think likely not. So that what we arrive at when we try to work from a purely chemical standpoint might be entirely unsuited to a given commercial case.

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## IMPROVEMENTS ON DR. SQUIBB'S VOLUMETRIC METHOD FOR ESTIMATING ACETONE.

BY LYMAN F. KEBLER.

Received February 13, 1897.

IN the December<sup>1</sup> number of this Journal Dr. Squibb gave a translation of MM. J. Robineau<sup>2</sup> and G. Rollin's method for estimating acetone, as well as a modification of the process by himself. Both methods consist essentially in mixing an aqueous acetone solution with a strongly alkaline potassium iodide solution and converting the acetone into iodoform by means of a titrated solution of sodium hypochlorite, the end reaction being determined by means of a bicarbonated starch solution.

Dr. Squibb kindly sent me his modification last summer. Prior to that time I had used Messinger's process exclusively. I have not applied Robineau and Rollin's method to any extent, but have studied and worked with Dr. Squibb's modification of the same quite considerably.

The two latter methods will meet with two objections; first, a *pure acetone*, and second, the tedious, time-consuming drop end reaction. Pure acetone is not so readily prepared. I have not been able to secure acetone that assayed more than 99.73 per cent. of pure material, by either Messinger's<sup>3</sup> process or the one presently to be described. This small quantity may have volatilized in course of the work, but the loss would be practically constant for all the methods; consequently, the basis of calculation would be 100, when in reality it is less. Grant that absolutely pure acetone can be made, it is not readily secured when desired.

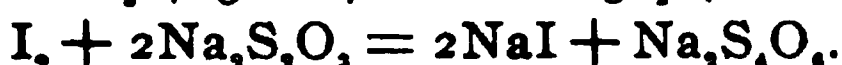
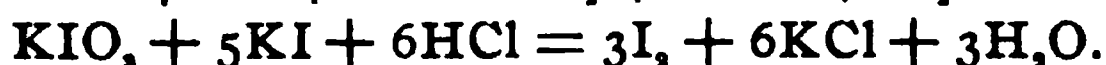
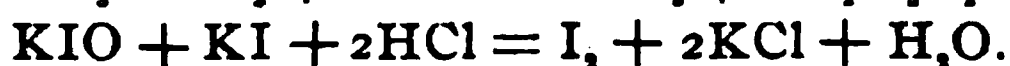
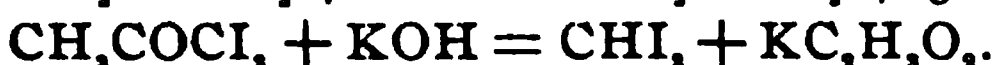
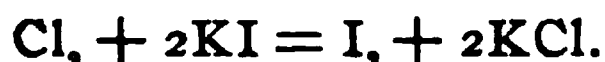
I have modified Dr. Squibb's method so that both the pure

<sup>1</sup> This Journal, 18, 1068; *Ephemeris*, 4, 1759.

<sup>2</sup> 1893: *Mon. Sci.*, (4), 7, Pt. I, 272.

<sup>3</sup> 1888: *Ber. d. chem. Ges.*, 21, 3366.

acetone and the drop end reaction are eliminated. The reactions involved in this process may be represented by the following equations:



There may be some difference of opinion concerning the primary reactions involved, but the basis of calculation is not affected.

The solutions required for this process are as follows:

1. A six per cent. solution of hydrochloric acid.
2. A decinormal solution of sodium thiosulphate.
3. An alkaline potassium iodide solution. To prepare, dissolve 250 grams of pure potassium iodide in distilled water and make up to one liter. Dissolve 257 grams of sodium hydroxide, purified by alcohol, in distilled water and make up to one liter. Allow the insoluble part to subside and mix 800 cc. of the clear solution with the liter of potassium iodide.
4. Sodium hypochlorite solution, about four-fifths normal, or containing from two and six-tenths to three per cent. of available chlorine. To prepare this solution, intimately mix 100 grams of bleaching powder (thirty-five per cent.) with 400 cc. of water. Dissolve 120 grams of crystallized sodium carbonate in 400 cc. of hot distilled water, and immediately pour the latter into the former. Cover the vessel and allow to cool. Then decant the clear liquid, filter the remainder, and to the filtrate add enough water to make up to one liter. To each liter add twenty-five cc. of sodium hydroxide solution, specific gravity 1.29.
5. An aqueous acetone solution containing from one to two per cent. of acetone. This is prepared by weighing the acetone in a beaker containing water, transferring to a graduated cylinder, rinsing the beaker with water and making up to a definite volume.
6. Bicarbonated starch solution. Treat 0.125 grams of starch with five cc. of cold water, then add twenty cc. of boiling water,

and boil a few minutes, cool, and add two grams of sodium bicarbonate.

Having prepared the above solutions, place twenty cc. of the alkaline potassium iodide solution into a suitable flask, add ten cc. of the diluted aqueous acetone; or weigh if greater accuracy is desired; mix well, and run in from a burette, while rotating the flask, an excess of the sodium hypochlorite solution, insert the stopper quickly and shake well for one minute. After agitating, render the mixture acid, by means of the hydrochloric acid solution, add, while rotating the flask, an excess of sodium thiosulphate solution, mix well and allow the mixture to stand a few minutes. Then add the starch indicator and re-titrate the excess of sodium thiosulphate. It is best to add a drop of the sodium hypochlorite in excess and adjust the final reading by means of the sodium thiosulphate.

The relation of the sodium hypochlorite solution to the sodium thiosulphate solution being known, the percentage of acetone can readily be calculated from the above data. One atom of available chlorine will liberate one atom of iodine from the potassium iodide of the alkaline solution, or one cc. will liberate just enough iodine to make one cc. of the same normal strength as the sodium hypochlorite solution originally was; therefore by reading the number of cc. of sodium hypochlorite solution consumed as so many cc. of iodine solution of the same normal strength, we reduce the calculation to the basis of iodine. One molecule of acetone (58) requires three molecules of iodine (759) to form one molecule of iodoform. Expressing it in the form of a proportion, letting  $y$  equal the amount of combined iodine and  $x$  equal the amount of acetone, we have:  $759 : 58 :: y : x$ , or  $x = y \frac{58}{759}$ , or  $x = y \cdot 0.07641$ .

*Example of Calculation.*—Ten cc. of the acetone solution, containing one gram of the solution to be analyzed required 14.57 cc. of  $N \times 0.806$  sodium hypochlorite solution, which formed 14.57 cc. of iodine solution of the same strength; or combining we have  $\frac{14.57 \times 0.806 \times 0.1265 \times 0.07641}{\text{one gram of solution}} = \text{amount of acetone} = 11.351 \text{ per cent.}$

On comparing Messinger's and Dr. Squibb's with the modified

method proposed, using the same solutions, the following results, in per cent. were obtained :

	Messinger.	Squibb.	Kebler.
Pure acetone.....	99.69	99.95	99.73
Residue 80° C. and above....	20.00	19.67	20.39
Purified acetone by fra'tion .	99.03	99.00	99.41
Commercial acetone.....	96.23	96.00	96.63
“ “ .....	98.00	97.83	97.93
“ “ .....	94.30	94.00	94.46
“ “ .....	94.80	94.70	94.81
“ “ .....	97.12	96.23	96.42
“ “ .....	94.93	94.80	94.39
“ “ .....	96.88	96.56	96.79
“ “ .....	97.32	97.28	97.45
“ “ .....	90.74	89.03	90.51
“ “ .....	98.82	96.11	98.62
“ “ .....	92.32	92.20	92.94
Wood alcohol.....	14.61	14.49	14.78
“ “ .....	11.81	11.73	12.00
Crude wood alcohol.....	11.23	11.00	11.42

The above table clearly shows that the results obtained by Dr. Squibb's process are a trifle too low, notwithstanding the fact that its basis of calculation gives it some advantage. The method is represented to give satisfactory results for ordinary work and that it certainly does. The difficulty with the process is in the end reaction. According to some experiments made by me, it is necessary to have present a larger excess of the active agent, to bring about the completed reaction, than the end reaction allows.

The iodoform reaction with ethyl alcohol is an endothermic one, consequently its presence does not interfere with the estimation of acetone, which does not require the presence of external heat to bring about the reaction.

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[CONTRIBUTIONS FROM THE CHEMICAL DIVISION, U. S. DEPARTMENT OF AGRICULTURE, No. 25.]

## DETERMINATION OF POTASH AND PHOSPHORIC ACID IN FODDERS.

CONTRIBUTED BY H. W. WILEY.

Received January 26, 1897.

IN the comparative analyses of soils during the past three years we have grown a great number of pot cultures and determined the mineral plant foods in the resulting crops. The following modified potash method, devised by Mr. K. P. McElroy, while not sacrificing accuracy, has made it possible for one analyst to determine the potash, often in duplicate, in more than ten samples a day. Since the quantity of the crop harvested from a poor soil is often small, it is desirable that the phosphoric acid and potash be determined in the same sample.

The method in use for the determination of potash in feeding stuffs, in the laboratory of the United States Department of Agriculture is a simple modification of the ordinary Lindo-Gladding method, as prescribed by the Association of Official Agricultural Chemists. It is as follows :

Burn eight grams of the substance over a low flame to approximate whiteness. Burning after addition of sulphuric acid does not give more potash than burning alone, and it is more troublesome. Transfer the ash to a 200 cc. flask, using about fifty cc. of water, add five cc. of strong hydrochloric acid and place on the steam-bath for an hour, or boil from five to ten minutes. Add a little iron chloride to precipitate all phosphoric acid as fer-



ric phosphate, then ten cc. of strong ammonia and then from five to ten cc. of ammonium carbonate solution (200 grams per liter of the commercial salt). Replace on the steam-bath and heat for an hour, and allow to stand over night. Complete the volume to the 200 cc. mark with water and shake three times at intervals of five or ten minutes. Grease the inside of the neck of the flask and pour its contents on a dry folded filter. When all is transferred to the filter and run through, wash down the neck of the flask with a little water, put the funnel into the flask, and stand aside till the filter dries. Then roll up the filter and push down into the flask. Add dilute nitric acid, digest, make volume up to the mark, and use an aliquot part for the determination of phosphoric acid.

Transfer fifty cc. of the filtrate containing the potash, equivalent to two grams of material, to a platinum dish, cover and heat on the steam-bath till evolution of gas ceases. Remove the cover and rinse it and the sides of the dish with a stream from the wash bottle. Evaporate to dryness and heat in an air-bath till all water is removed in order to avoid loss by decrepitation in the subsequent ignition. Heat over a low gas flame till the bulk of the ammonium chloride is removed, cool and add one cc. of sulphuric acid (1 : 1), then heat on a hot plate till fuming begins, then over a flame till all the sulphuric acid is driven off and the residue in the dish is white. Every portion of the dish should reach a low but distinct red heat, the bottom first and then the sides. The reason for the preliminary driving off of the bulk of the ammonia as sal-ammoniac is that ammonium sulphate melts and sputters, involving danger of loss. Cool the dish and add one or two drops of strong hydrochloric acid, then from fifty to seventy-five cc. of water, washing down the sides of the dish with a jet from the wash bottle. Add platinum chloride solution in amount equivalent to 150 mm. of metallic platinum, for materials not containing over four per cent. of potash. Very few reach this limit. Evaporate on the water-bath as usual and take up with alcohol of eighty (volume) per cent. Filter through a Gooch crucible, keeping the insoluble material in the dish as far as possible. Wash with four more portions of alcohol, decanting through the crucible each time. Finally rinse down the sides of the crucible with a stream of alcohol from a

wash bottle. Cover the residue in the dish with the half-saturated solution of ammonium chloride prescribed in the official method for the determination of potash, and stir thoroughly. Decant through the Gooch crucible and treat with five or more portions of sal-ammoniac solution, decanting through the crucible each time. Finally wash into the crucible with eighty per cent. alcohol. When the transfer is complete, rinse the sides of the crucible thoroughly and finally fill it twice with alcohol, of course, constantly filtering with a vacuum. Dry for an hour at  $100^{\circ}$  and weigh.

Pour about 150 cc. of boiling water through the weighed Gooch crucible. If the platinum potassium chloride is not wholly dissolved, again bring the filtrate to a boil and pour through once more. Store this filtrate finally in a large flask, containing aluminum clippings, to reduce the platinum. Bring a fresh portion of water (150 cc.) to a boil and pour through the Gooch crucible. Remove the crucible from the vacuum apparatus, wipe, and dry in an air-bath, with good ventilation, for two hours, at  $110^{\circ}$ . Weigh once more. The loss in weight is the double chloride. The second portion of hot water is used to dissolve the double salt in the next crucible operated upon, after being once more brought to a boil.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF MICHIGAN.]

### PERIODIDES OF PYRIDINE.<sup>1</sup>

BY P. F. TROWBRIDGE.

Received February 1, 1897.

*Pyridine Methyl Pentiodide*,  $C_5H_5N.CH_3.I.I_4$ .—This preparation has been reported,<sup>2</sup> but the present method of preparation is of interest. It was obtained in two experiments, when pyridine was added to an alcoholic solution of iodine containing methyl iodide. The precipitate of the pyridine tetriodide<sup>3</sup> was filtered off and the liquor set aside for partial evaporation. The crystals obtained were purified by recrystallizations from alcohol. Melting-point  $44.5^{\circ} C$ .

	Calculated for $C_5H_5N.CH_3.I.I_4$ .	Found.	
		1.	2.
Total iodine <sup>3</sup> .....	87.06	86.24	87.19
Titrated iodine.....	69.65	69.64	69.21

<sup>1</sup> Continuation of paper by Prescott and Trowbridge. This Journal, 17, 859.

<sup>2</sup> This Journal, 17, 859.

<sup>3</sup> This Journal, 17, 867, for methods of analysis.

*Pyridine Methyl Heptiodide*,  $C_5H_5N.CH_2I.I_6$ .—A provisionally named octaiodide was reported,<sup>1</sup> but it is very probable that it was a mixture of the heptiodide with some free iodine. In the present experiment, the iodine was taken in great excess to the pyridine methyl iodide; *i.e.*, sufficient for twelve atoms of additive iodine. The pyridine methyl iodide and the iodine were mixed when in the form of hot saturated alcoholic solutions. The mixture was kept hot for fifteen minutes. A heavy dark-green oil formed, which was rapidly separated. This became a crystalline solid at about 20° C. and melted when warmed above 30° C. Insoluble in water, but soluble in dilute alcohol, from which it crystallizes in fine green needles, which are fairly stable. Melting-point 26° C.

	Calculated for $C_5H_5N.CH_2I.I_6$ .	Found. 1.	2.
Total iodine .....	90.40	90.36	90.23
Titrated iodine.....	77.48	77.31	78.21

The liquor from the above was found to contain the pentiodide not entirely pure.

At the present writing we have not succeeded in preparing a higher periodide of pyridine methyl iodide. When pyridine methyl iodide is heated in sealed tubes to 125° C. with an alcoholic solution of iodine, the pentiodide is formed. When the same mixture is heated to 175° C. ethyl iodide is formed and no definite periodide could be isolated. When pyridine methyl iodide and iodine are heated in tubes to 200° C. without the addition of alcohol, the heptiodide is formed. This product was purified by recrystallization from alcohol. Melting-point 26.5° C. Reported as 2 above.

When pyridine and iodine are heated to 175° C. the tetriodide is formed.

*Pyridine Ethyl Pentiodide*,  $C_5H_5N.C_2H_5I.I_5(?)$ .—When pyridine, iodine, and alcohol are heated in tubes to 175° C., a pasty mass is formed having a carbonaceous odor. Definite black crystals were obtained by treatment with alcohol. Melting-point 83° C.

	Calculated for $C_5H_5N.C_2H_5I.I_5$ .	Found.
Total iodine .....	85.41	86.32
Titrated iodine .....	68.33	68.59

The corresponding methyl compound melts at about 44° C.<sup>1</sup>

<sup>1</sup> This Journal, 17, 859.

This ethyl compound should melt below  $44^{\circ}$  C., as the normal ethyl iodide melts at a much lower temperature than the methyl compound.<sup>1</sup> It is quite possible that ethyl iodide is first formed, which combines with the pyridine; and then, under the pressure and heat, the Ladenburg reaction takes place and ethyl pyridine hydriodide tetriodide,  $C_5H_5(C_2H_5)N.HI.I_3$ , is formed. Pyridine ethyl triiodide (described later in this paper) also melts at  $51^{\circ}$  C. Pyridine ethyl pentiodide must melt at a lower temperature. Further investigation will be made of this preparation.

To find, if possible, the limit of iodine addition to pyridine methyl iodide, the following series of experiments was made. A definite amount of carefully purified pyridine methyl iodide,  $C_5H_5N.CH_3I$ , was dissolved in a small amount of alcohol, and to this a cold saturated alcoholic solution of iodine was added. The amount was taken so that in (1) there was just sufficient iodine for one atom of additive iodine; in (2) just enough for two atoms of additive iodine; etc. In this series of experiments the solutions were not warmed. All were treated at the temperature of ordinary summer weather.

1. No crystals formed in twenty-four hours. On cooling in salt and ice an abundance of red needle-like crystals was obtained. These were purified from alcohol. Melting-point  $49^{\circ}$  C.

	Calculated <sup>2</sup> for $C_5H_5N.CH_3I.I$	Calculated for $C_5H_5N.CH_3I.I_2$	Found.
Total iodine.....	72.91	80.14	79.26
Titrated iodine.....	36.46	53.43	52.11

2 and 3. Crystals formed at once, and upon purification gave handsome, overlapping, reddish-brown plates. Melting-point  $50^{\circ}$  C.

	Calculated for $C_5H_5N.CH_3I.I_2$	2.	Found. <sup>2</sup> 3.
Total iodine.....	80.14	79.46	79.59
Titrated iodine....	53.43	53.09	53.08

4. A heavy green oil formed at once, which became a semi-solid green mass upon standing. This was purified from alcohol. Short greenish needles were obtained. Melting-point  $44^{\circ}$  C. From the liquor, after removal of the oil, crystals were

<sup>1</sup> This Journal, 18, 91.

<sup>2</sup> This Journal, 17, 860.

obtained, which, upon purification, gave the reddish-brown plates. Melting-point  $50^{\circ}$  C.

	Calculated for $C_5H_5N.CH_2I.I_2$	Calculated for $C_5H_5N.CH_2I.I_4$	Found.	
			Oil.	Liquor.
Total iodine.....	80.14	87.06	86.12	79.40
Titrated iodine..	53.43	69.65	66.47	53.13

5. A dark-green oil formed at once, forming crystals upon purification. Analysis gave 85.73 per cent. of total iodine and 66.76 per cent. of titrated iodine. From the liquor more oil was obtained, which also gave crystals upon purification. Analysis gave 80.17 per cent. of total and 63.80 per cent. of titrated iodine. In both the above cases the crystals were not sharply defined, nor were they of definite melting-points. Theory as  $C_5H_5N.CH_2I.I_2$  gives 84.33 per cent. of total and 63.25 per cent. of titrated iodine.

6. Results very similar to those in (5) were obtained, except no crystals whatever could be secured from the first oil. Green needles were obtained from the liquor. Iodine found, 86.30 per cent. total and 70.08 per cent titrated.

7. The green oil which formed at once gave the dark-green needles upon crystallization from alcohol. Melting-point  $44^{\circ}$  C. Found 86.50 and 68.56. From the liquor dark-green crystals were obtained. Melting-point  $45^{\circ}$  C. Found 85.92 and 70.08.

8. A dark-green oil formed at once. This was purified. Found 86.31 and 69.51. In the liquor long dark-green needles formed on standing over night. These were analyzed without further purification. Melting-point  $44.5^{\circ}$  C. Found 86.57 and 68.24.

9. As in 8. Melting-point  $44.5^{\circ}$  C. Found from oil 86.88 and 69.17 ; from liquor 86.81 and 68.99.

10. The dark-green oil would not crystallize from alcohol. The liquor gave very long (three inches) dark-green needles. These were analyzed without further purification. Melting-point  $44^{\circ}$  C. Found 86.26 and 68.87.

The following table gives a brief summary of the results in the series above described :

		Melting-point.	Total iodine.		Titrated iodine.		Calculated for
			Found.	Theory.	Found.	Theory.	
1		49	79.26	80.14	52.11	53.43	$C_5H_5N.CH_3I.I_2$
2		50	79.46	80.14	53.09	53.43	$C_5H_5N.CH_3I.I_2$
3		..	79.59	80.14	53.08	53.43	$C_5H_5N.CH_3I.I_2$
4		44	86.12	87.06	66.47	69.65	$C_5H_5N.CH_3I.I_4$
4	liquor	50	79.40	80.14	53.13	53.43	$C_5H_5N.CH_3I.I_2$
5		..	85.73	84.33	66.76	63.25	$C_5H_5N.CH_3I.I_2$
5	"	..	80.17	84.43	63.80	63.25	$C_5H_5N.CH_3I.I_2$
6		..	....	....	....	....	
6	"	..	86.30	87.06	70.08	69.65	$C_5H_5N.CH_3I.I_4$
7		44	86.50	87.06	68.56	69.65	$C_5H_5N.CH_3I.I_4$
7	"	45	85.92	87.06	70.08	69.65	$C_5H_5N.CH_3I.I_4$
8		..	86.31	87.06	69.51	69.65	$C_5H_5N.CH_3I.I_4$
8	"	44.5	86.57	87.06	68.24	69.65	$C_5H_5N.CH_3I.I_4$
9		44.5	86.88	87.06	69.17	69.65	$C_5H_5N.CH_3I.I_4$
9	"	..	86.81	87.06	68.99	69.65	$C_5H_5N.CH_3I.I_4$
10		..	....	....	....	....	
10	"	44	86.26	87.06	68.87	69.65	$C_5H_5N.CH_3I.I_4$

In further studying the limits of iodine addition with pyridine methyl iodide, another series of experiments was made, in which pyridine was added to an alcoholic solution of iodine containing methyl iodide. The iodine was so taken that (1) gave iodine for one additive atom, (2) for two, etc., temperature conditions being the same as in the preceding series. In all cases there was formed at first the pyridine tetriodide, which was rapidly separated by filtration and the liquor set aside for evaporation and crystallization. The products obtained were purified by recrystallization and then carefully analyzed.

(1) and (2) gave a mixture of the pyridine methyl diiodide and triiodide. (3) gave the triiodide in most excellent conditions of purity. (4) and (5) gave the pentiodide very pure..

From the above series of experiments we must conclude that, at ordinary temperature and with small amounts of iodine, the triiodide is usually formed, and with larger amounts of iodine the pentiodide; and this latter is the highest periodide that will form of pyridine methyl iodide at ordinary temperature, no matter how much iodine be used. Some of the preparations are evidently mixtures of the triiodide and the pentiodide. There is no satisfactory evidence of the formation of a pyridine methyl tetriodide.

*Pyridine Hydriodide*,  $C_5H_5N.HI.H_2O$ .—White needle-like

crystals, soluble in water and alcohol, insoluble in ether, melt at about  $268^{\circ}$  C. with some decomposition. Upon standing, the crystals become brownish in color and after a few days give off pyridine. Dilute hydriodic acid freshly distilled from red phosphorus was added to pyridine diluted with water. The crystals were obtained by partial evaporation and then cooling. These were purified by crystallizing from water and drying over sulphuric acid.

0.4501 gram gave 0.4728 gram silver iodide, or 0.2554 gram iodine, or 56.74 per cent. iodine.

Theory for  $C_5H_5N.HI.H_2O = 56.34$  per cent.

Theory for  $C_5H_5N.HI = 61.25$  per cent.

*Pyridine Hydriodide*,  $C_5H_5N.HI$ .—This preparation has the same properties as that just described. It is made by adding freshly distilled hydriodic acid, sp. gr. 1.96, to pure pyridine cooled in a mixture of salt and ice. The pure white crystals formed at once and were purified by washing repeatedly with absolute ether. After being thus purified they do not take up a molecule of water when recrystallized from water. Neither the salt purified by washing with ether nor that crystallized from water loses an appreciable amount on being heated for six hours at  $100^{\circ}$  C.

Iodine found before drying.	Iodine found after drying six hours.	Theory for $C_5H_5N.HI$ .
61.21	60.88	61.25
60.93	60.65	....
61.00	....	....

*Pyridine Hydrogen Diiodide*,  $C_5H_5N.HI.I$ .—Dark-brown short needles, perfectly stable, slightly soluble in water, very soluble in alcohol. Melting-point  $188^{\circ}$ – $192^{\circ}$  C. Crystallizes from absolute alcohol as brown overlapping plates. This preparation was made (1) by treating pyridine with hydriodic acid containing some free iodine, and then allowing to stand; (2) by adding an alcoholic solution of iodine to pure pyridine hydriodide in the cold.

	Found.		Calculated for $C_5H_5N.HI.I$ .
	1.	2.	
Total iodine.....	75.66	75.75	75.97
Titrated iodine.....	37.32	37.95	37.98
	....	37.93	....
	....	37.94	....

*Hollow Crystals of the Pyridine Hydrogen Diiodide.*—The liquor from the first crystallization of the  $C_5H_5N.HI.H_2O$ , was treated with an alcoholic solution of iodine (not a great excess), and allowed to stand for twenty-four hours. A large bulk of crystals was obtained, fully fifty grams. They were reddish-brown hexagonal hollow prismatic crystals of very uniform size and many of them fully two inches long. Melting-point  $188^{\circ}$ – $191^{\circ}$  C. These crystals are the pyridine hydrogen diiodide but not quite pure. Analytical results are about one per cent. too low, both in total and titrated iodine. When these hollow crystals are recrystallized from alcohol the pure diiodide is obtained in fine needle-like crystals. I have tried repeatedly to reproduce the hollow crystals, but without success. Hollow crystals have been reported by Kebler.<sup>1</sup>

*Pyridine Hydrogen Pentiodide*,  $C_5H_5N.HI.I_4$ .—Stable, very dark, brownish-black, short crystals, melting-point  $78^{\circ}$ – $82^{\circ}$  C. Obtained (1) from the liquor of the heptiodide described below, by evaporation and several recrystallizations from alcohol; (2), by dissolving iodine in hydriodic acid, warming, and adding a calculated quantity of pyridine. Crystals form and are purified from alcohol, in which they are very soluble.

	Found.		Calculated for $C_5H_5N.HI.I_4$ .
	1.	2.	
Titrated iodine.....	71.09	69.91	71.01
Total iodine.....	....	87.66	88.77

*Pyridine Hydrogen Heptiodide*,  $C_5H_5N.HI.I_6$ .—Lustrous green scales, fairly stable, soluble in alcohol, melting-point  $63^{\circ}$ – $64^{\circ}$  C. Hydriodic acid was added to pyridine and then heated on the water-bath. To this a hot saturated alcoholic solution of iodine was added. An abundance of crystals was obtained upon cooling. Purified by recrystallization from alcohol.

	Found.	Calculated for $C_5H_5N.HI.I_6$ .
Total iodine .....	92.23	91.71
Titrated iodine .....	78.65	78.67

Not being successful in any of the previous experiments in making pyridine hydrogen triiodide, a series of experiments was started, from which it was hoped to obtain the desired periodide. Pure pyridine hydriodide was dissolved in dilute alcohol, and iodine in alcoholic solution was added. (1) contained

<sup>1</sup> *Am. J. Pharm.*, 67, 602.



iodine sufficient for one-half atom of additive iodine, (2) for one atom, (3) two atoms, (4) three atoms, (5) four atoms, (6) five atoms, (7) six atoms, (8) seven atoms, (9) ten atoms, and (10) fifteen atoms.

In (1) to (6) no heat was used, in the others the solution of pyridine hydriodide was heated and the iodine added as a hot saturated alcoholic solution.

(1). After several crystallizations the pure  $C_5H_5N.HI.I$  was obtained in needles one-half inch long.

(2). Same as (1).

(3). Same as (1), but impure.

(4) and (5).  $C_5H_5N.HI.I_2$ , but impure.

(6).  $C_5H_5N.HI.I_2$ , pure.

(7).  $C_5H_5N.HI.I_2$ , pure.

(8), (9), and (10).  $C_5H_5N.HI.I_2$ , fairly pure in each case.

Thus far we have been unable to make the triiodide,  $C_5H_5N.HI.I_3$ . The corresponding periodides of the methyl and ethyl series are very easily made.

*Pyridine Ethyl Triiodide*,<sup>1</sup>  $C_5H_5N.C_2H_5.I_3$ .—To 23.4 grams pure pyridine ethyl iodide dissolved in a small amount of alcohol, 12.6 grams of iodine dissolved in alcohol were added. No crystals formed on standing twenty-four hours, lightly covered, but after a second twenty-four hours, several large clusters of crystals were formed. These are bluish-black, thin, rhomboidal, overlapping plates. Melting-point  $51^\circ C$ .

In a second preparation a greater quantity of iodine was taken and the pure crystals obtained free from adhering oil by several recrystallizations. Melting-point  $51^\circ C$ . In a third and fourth preparation the above periodide was made in the attempt to make pyridine ethyl chloride periodide. A water solution of pyridine ethyl iodide was shaken with a slight excess of freshly precipitated silver chloride until the filtrate gave no test for iodine. This filtrate was treated with a potassium iodide solution of iodine. A heavy black oil formed, which was carefully separated and placed in tightly stoppered bottles. Owing to other work, these stood for three months. The oily products had become crystalline with some adhering oil. The crystals were very compact, hard, lustrous, and greenish-black.

<sup>1</sup> This Journal, 17, 862.

Careful tests showed entire absence of chlorine. They were recrystallized from absolute alcohol, when lustrous, greenish-black, overlapping plates were formed. Some of these plates are fully one inch long, with very definite angles. Melting-point, (3),  $52^{\circ}$  C., (4),  $51^{\circ}$  C.

	Found.				Calculated for $C_5H_5N.C_2H_5I.I_2$
	1.	2.	3.	4.	
Total iodine .....	77.91	77.68	78.33	....	77.85
	77.27	77.57	....	....	....
Titrated iodine ...	50.77	51.83	52.42	52.15	51.90
	51.48	51.91	51.80	51.80	....
	51.06	....	51.86	....	....

Work is being continued on periodides of quinoline piperidine and mixed perhalides of pyridine and quinoline.

*Molecular Weight Determinations.*—Much difficulty has been experienced in determining the probable molecular composition of the pyridine periodides. Since alcohol is such a ready solvent for them and heat so readily decomposes them, it was deemed advisable to try the vapor-tension method of Will and Bredig.<sup>1</sup> We find that this method is not at all applicable to the perhalides, but as a check on our own work, we very easily confirmed Will and Bredig's work on nitrobenzene.

The freezing-point method was tried, using nitrobenzene, formic acid, glacial acetic acid, and phenol. None of these solvents seem to decompose the perhalides, but phenol is the only solvent that gives sufficient deviation of the freezing-point.

	Found.	Theory.
$C_5H_5N.HI.I$ .....	387	
	375	
	386	333
	398	
$C_5H_5N.CH_2I.I$ .....	398	
	334	347
$C_5H_5N.C_2H_5I.I_2$ .....	403	
	423	487
$C_5H_{11}N.CH_2I.I_2.H_2O$ .....	496.8	497.5
$C_5H_5N.CH_2I.I_4$ No accurate results.		

It is of much significance that two different diiodides, having but one atom of additive iodine to one atom of normal iodine, are clearly found to be monopyridine compounds, the same as those with even numbers of additive iodine. It would appear, therefore, that in the diiodides one of the two iodine atoms exer-

<sup>1</sup> *Ber. d. chem. Ges.*, 22, 1084.

cises an even valence, as in  $C_6H_5N \begin{smallmatrix} R \\ \diagdown \\ I-I \end{smallmatrix}$ , or perhaps

$C_6H_5N \begin{smallmatrix} R \\ \diagdown \\ I=I \end{smallmatrix}$ . With the higher perhalides the burden of experiment points very strongly to the formation of compounds having only an even number of additive halogen atoms. The

structure may be<sup>1</sup>  $C_6H_5N \begin{smallmatrix} R \\ \diagdown \\ I \begin{smallmatrix} I-I \\ | \quad || \\ I-I \end{smallmatrix} \end{smallmatrix}$ , etc., at all events indica-

ting uneven valence for all halogen atoms. It is quite probable that all the pyridine perhalides exist in monopyridine molecules.

If there be an analogy between the perhalides of the tertiary amines and the ammonium salts of the oxyacids of chlorine, then

the structure may be  $\equiv N \begin{smallmatrix} R \\ \diagdown \\ (I=I)-I \end{smallmatrix}$ ,  $\equiv N \begin{smallmatrix} R \\ \diagdown \\ (I=I)-I \begin{smallmatrix} I \\ || \\ I \end{smallmatrix} \end{smallmatrix}$ ,

etc., where  $(I=I) = O$ . In this case the single additive halogen would be divalent and a substitute for oxygen, *i. e.*,

$\begin{smallmatrix} H \\ H \\ H \end{smallmatrix} = N \begin{smallmatrix} H \\ \diagdown \\ O-Cl \end{smallmatrix}$  and  $\equiv N \begin{smallmatrix} R \\ \diagdown \\ I-I \end{smallmatrix}$ . In the mixed perhalides to be reported in a later paper, the single additive halogen is of more frequent occurrence.

I wish to express my thanks to Professor A. B. Prescott, to whom I have gone for advice and under whose general supervision the work has progressed; also to Messrs. O. C. Diehl<sup>2</sup> and R. E. Knapp for their assistance in the laboratory.

ANN ARBOR, MICH., Jan. 23, 1897.

## MODIFICATION OF THE THALLEOQUIN TEST FOR QUININE.

BY F. S. HYDE.

Received February 12, 1897.

It is extremely important for the success of this test that the reagents employed should be dilute. Some authorities give the quantity of each reagent necessary, without stating the proper dilution, thereby causing much inconvenience.

The light green coloration produced on porcelain by contact of the quinine salt with weak bromine or chlorine water and

<sup>1</sup> This Journal, 17, 780.

<sup>2</sup> This is the beginning of Mr. Diehl's work upon "Foundations for the Estimation of Alkaloids, Conducted for the Committee of Revision of the U. S. Pharmacopeia," by Prof. A. B. Prescott. The next following work has been upon "Mixed Perhalides of Pyridine and Piperidine," now nearly ready for publication.

ammonia is not nearly so striking as the brilliant emerald green color obtained by using dilute solutions in a test-tube.

Usually, the analyst deals with unknown quantities, or mere traces, but, for experiment, it will be found convenient to use from three to five milligrams of the quinine salt for each test. (With larger amounts there is a tendency to form bulky precipitates.)

For example, place three to five milligrams (0.003–0.005 gram) quinine sulphate in a test-tube and add about five cc. distilled water. Acidulate with *one* drop (not more) of dilute sulphuric acid (1 : 4) which immediately dissolves the quinine sulphate with a blue fluorescence. An excess of the acid should be avoided.

At this point various authorities recommend the addition of weak bromine or chlorine water ; but the writer has found that if a clear, filtered solution of calcium hypochlorite (bleaching powder) be substituted for the bromine or chlorine water, the results will be more satisfactory so far as certainty and brilliancy of the test are concerned.

The points to be observed are as follows : After acidulation with one drop of sulphuric acid (1 : 4), the hypochlorite solution is added through a small filter to the quinine solution in the test-tube, until the blue fluorescence just disappears, and the solution acquires a faint golden tint ; then add a few drops of dilute ammonia (1 : 3) when a clear emerald green color should appear. (Thalleoquin test.)

The tint, thus produced, seems to be more brilliant than that obtained through the agency of bromine water.

On the addition of a slight excess of dilute sulphuric acid to this green solution, a blood-red tint will be produced which may be considered confirmatory. This is not always the case, however, when bromine water has been used in the preliminary operation.

Potassium or sodium hypobromite is not applicable on account of the strong alkali which tends to precipitate the white quinine base and thus interfere with the brilliancy of the test. Chlorinated soda (Labarraque's solution) likewise gives uncertain results, the tints varying from yellowish-green to violet.

## COMPOUNDS OF METALLIC HYDROXIDES WITH IODINE.

BY THEODORE RETTIE.

Received March 1, 1897.

SCHLAGDENHAUFFEN<sup>1</sup> describes a method for the quantitative determination of magnesium in a solution containing barium, strontium and calcium without previously removing these metals. He employed a reagent prepared by adding iodine to a two per cent. solution of potassium hydroxide, in sufficient quantity to produce a golden yellow solution. This reagent gives, even with very dilute solutions of magnesium salts, a dark, reddish-brown precipitate. An apparently similar precipitate was obtained by the same author by adding iodine, dissolved in potassium iodide solution, to a solution of a magnesium salt and then cautiously adding potassium hydroxide solution. Excess of the latter reagent entirely decolorizes the precipitate, leaving magnesium hydroxide. The nature of the brown precipitate does not seem to have been determined by Schlagdenhauffen, and therefore it appeared of interest to examine it with a view to ascertaining if it is of constant composition.

In order to prepare quantities of the precipitate, solution of magnesium sulphate was mixed with enough solution of iodine in potassium iodide to impart to it a dark brown color. Potassium hydroxide solution was then added in sufficient quantity to produce a bulky precipitate, leaving the solution still dark-brown. The brown precipitate, when filtered off and sucked as dry as possible, if washed with hot water, loses all its color and decreases considerably in bulk, leaving a white residue of magnesium hydroxide. The washings are colorless, neutral to test papers, and give the reactions of magnesium and of iodides. Cold water acts on the precipitate in a similar manner, but only very slowly. If washed with water saturated with iodine, no iodide is dissolved out, as was determined by titrating the aqueous solution of iodine before and after the washing. When exposed to the air the dry precipitate loses iodine very slowly; dried in a vacuum no iodine is lost. This was proved quantitatively by determining the ratio of iodine to magnesium in some of the freshly precipitated substance, and then in the same precipitate when dried in a vacuum; in both cases the ratio was the same.

<sup>1</sup> *J. Pharm. Chem.* (4), 27, 375.

A portion of the moist precipitate gave on analysis :

0.0330 gram silver iodide, or 0.0178 gram iodine, and 0.0771 gram magnesium pyrophosphate, or 0.0168 gram magnesium.

Therefore  $I : Mg :: 1 : 4.9$ .

Dried in a vacuum, same precipitate gave 0.0289 gram iodine by titration, and 0.0452 gram magnesium oxide or 0.0272 gram magnesium.

Therefore  $I : Mg :: 1 : 4.9$ .

Chloroform, ether, alcohol, and potassium iodide all extract a little iodine from the dried precipitate, but none of them extract the whole of it. Sulphurous acid and sodium thiosulphate both decolorize the precipitate completely. The precipitate dissolves completely in acids, giving a solution colored brown by free iodine. On heating the dry substance to  $100^{\circ}C$ . water is given off, but no iodine; this fact was proved by a determination of the ratio of iodine to magnesium before and after heating. On ignition in a sublimate tube, the substance, previously heated to  $100^{\circ}C$ ., gives off water and then iodine, and if ignited strongly enough leaves pure magnesia. Advantage was taken of this latter reaction to obtain a quick method for determining the iodine and magnesium.

The substance was weighed in a platinum boat, ignited in a piece of combustion tubing, having one end drawn out and passed through an India rubber stopper so as to dip into a solution of sulphurous acid contained in a small flask. A current of air being sucked through the apparatus, the iodine is absorbed in the flask and can be determined either by adding dilute nitric acid to the sulphurous acid solution and precipitating with silver nitrate, or by employing instead of sulphurous acid a known quantity of standard thiosulphate solution and titrating back with standard iodine. The residue from the ignition in the tube contains a small quantity of iodine, which is given off on stronger ignition, leaving pure magnesia. The results of analyses of five different preparations are given below.

A. The ratio of iodine to magnesium was determined in some freshly precipitated substance. In a given weight there was found 0.0902 gram silver iodide, or 0.0487 gram iodine, and 0.1650 gram magnesium pyrophosphate, or 0.0361 gram magnesium.

$I : Mg :: 1 : 3.8$ .

B. Freshly precipitated gave ratio I : Mg :: 1 : 4.9 (as above).  
Dried in a vacuum,

	Per cent.
0.1008 gram substance gave 0.0452 gram MgO	= 44.84
0.0289 gram I	= 28.67
H <sub>2</sub> O by difference	= 26.49
	<hr/>
	100.00

I : Mg :: 1 : 4.9.

MgO : H<sub>2</sub>O :: 1 : 1.06.

C. The precipitate dried in a vacuum over sulphuric acid was heated to 100° C. in a steam cupboard till constant in weight. The iodine and magnesium were determined by the ignition method described above. The water was determined directly by ignition in a combustion tube, the iodine being absorbed by a red hot silver spiral and the water collected in a sulphuric acid tube.

Substance taken = 0.1185 gram.

	Per cent.
MgO = 0.0616 gram	= 51.98
I = 0.0307 gram	= 25.90

Water. Substance taken, 0.1990 gram.

H <sub>2</sub> O = 0.0430 gram	= 21.93
	<hr/>
	99.81

I : Mg :: 1 : 6.3.

H<sub>2</sub>O : MgO :: 1 : 1.05.

D. Dried *in vacuo* over sulphuric acid.

Substance taken = 0.0610 gram.

	Per cent.
MgO = 0.0300 gram	= 49.18
I = 0.0166 gram	= 27.21
H <sub>2</sub> O by difference	= 23.61
	<hr/>
	100.00

I : Mg :: 1 : 5.6.

MgO : H<sub>2</sub>O :: 1 : 1.07.

As it seemed probable that the low percentage of iodine in "C" might be due to loss of iodine on heating to 100° C., the ratio of iodine to magnesium was determined in the next preparation (E) both before and after heating to 100°.

E. This precipitate was produced under slightly different conditions from the former ones. A very large excess of iodine was employed and the precipitate was left standing for twenty-four hours in contact with an excess of iodine. The precipitate when filtered off and dried in a vacuum had a dark greenish-black appearance and yielded, on pounding up, a very dark purplish brown powder.

Precipitate dried in a vacuum.

Substance taken = 0.3584 gram.

	Per cent.
MgO = 0.1185 gram	= 33.06
I = 0.1759 gram	= 49.07
H <sub>2</sub> O by difference	= 17.87
	<hr/>
	100.00

I : Mg :: 1 : 2.1.

MgO : H<sub>2</sub>O :: 1 : 1.2.

Precipitate heated to 100° C. for three hours.

Substance taken = 0.3303 gram.

	Per cent.
MgO = 0.1130 gram	= 34.21
I = 0.1686 gram	= 51.04
H <sub>2</sub> O by difference	= 14.75
	<hr/>
	100.00

I : Mg :: 1 : 2.1.

H<sub>2</sub>O : MgO :: 1 : 1.03.

Collecting the above results we get the following ratios :

- A. I : Mg :: 1 : 3.8.
- B. I : Mg :: 1 : 4.9, MgO : H<sub>2</sub>O :: 1 : 1.06.
- C. I : Mg :: 1 : 6.3, H<sub>2</sub>O : MgO :: 1 : 1.05.
- D. I : Mg :: 1 : 5.6, MgO : H<sub>2</sub>O :: 1 : 1.07.
- E. I : Mg :: 1 : 2.1, H<sub>2</sub>O : MgO :: 1 : 1.03.

These results show that the precipitate is simply magnesium hydroxide with a variable quantity of iodine carried down with it, giving a body resembling the lakes. Aluminum acetate gives a similar precipitate, but not so stable as the magnesium one. Aluminum sulphate, however, will not react thus. Moist magnesium hydroxide (freshly precipitated and washed), on shaking up with iodine solution, takes up iodine, although more slowly than that precipitated in presence of the iodine, while it does not seem capable of taking up so much.



On trying the action of potassium hydroxide in presence of iodine on the salts of the other metals of the magnesium group, colored precipitates were formed with zinc and cadmium salts. Glucinum sulphate gave a dark-brown precipitate which dissolved upon standing; when more potassium hydroxide was added a precipitate of hydroxide formed. With strong solutions of calcium and strontium salts, a very peculiar reaction took place, a dark, greenish-brown precipitate being produced, which changed to reddish-brown, and on standing for a short time dissolved completely. Excess of potassium hydroxide gradually took the color out of the precipitate, but much more slowly than with magnesium. Barium salts do not react in this way at all. Lithium chloride behaves in a somewhat similar manner to calcium salts; a dark-brown precipitate is formed, which soon dissolves. On adding a little more potassium hydroxide, the same precipitate again forms and again dissolves up.

The cadmium and zinc precipitates are much more stable than the above. The cadmium precipitate (from cadmium nitrate), when filtered off and washed with water saturated with iodine, is very gelatinous and of a dark purple brown color; on drying in a vacuum it gradually loses its color till it becomes a pale buff, when no further change takes place. On heating this buff-colored powder in a platinum boat in a combustion tube, water and iodine were given off, leaving a brown residue of cadmium oxide; the oxide was dissolved in nitric acid and tested for iodine; none present.

The formation of the zinc precipitate depends on the salt used and also on the strength of the solution; neither the sulphate nor chloride gives the precipitate while the acetate does. When a solution containing forty grams zinc acetate per liter is employed, a brown flocculent precipitate is formed, which does not change on standing. If the brown precipitate be filtered off and dried in a vacuum, it gives off all its iodine, leaving a white powder. In a solution containing fifteen grams zinc acetate per liter, the brown flocculent precipitate at first formed takes up more iodine on standing with a large excess of iodine and becomes crystalline and of an olive green color. This green precipitate when filtered off and washed with water is not decomposed, but if left exposed to the air in a moist state rapidly turns

brown, losing iodine. Dried in a vacuum the precipitate is not decomposed. The dirty green powder thus obtained is not so stable as the magnesium compound; it smells of iodine, and when left exposed to the air gradually becomes white. When heated to  $100^{\circ}$  in a steam cupboard iodine vapor is given off. On ignition in a platinum boat in a combustion tube, water and iodine are given off first, then a small white sublimate of zinc iodide. As this prevented any speedy method of determining the zinc in the substance, the ordinary method of precipitation with sodium carbonate was employed. The difficulty of washing and drying large precipitates without decomposing them necessitated the employment of small quantities for analysis.

A. Substance taken = 0.0949 gram.

	Per cent.
ZnO = 0.0500 gram	= 52.68
AgI = 0.0485, or I = 0.0250 gram	= 27.61
Water determined directly (as in magnesium compounds.)	
Substance taken = 0.1724 gram.	
H <sub>2</sub> O = 0.0294 gram	= 17.05
	<hr/>
	97.34

I : Zn :: 1 : 2.9.

ZnO : H<sub>2</sub>O :: 1 : 1.4.

B. Substance taken = 0.0616 gram.

	Per cent.
ZnO = 0.0982 gram	= 48.80
AgI = 0.1150 gram, or I = 0.0621 gram	= 30.88
H <sub>2</sub> O by difference	= 20.32
	<hr/>
	100.00

I : Zn :: 1 : 2.5.

ZnO : H<sub>2</sub>O :: 1 : 1.9.

C. Substance taken = 0.3409 gram.

	Per cent.
ZnO = 0.1731 gram	= 50.77
AgI = 0.2035 gram, or I = 0.1094 gram	= 32.09
H <sub>2</sub> O by difference	= 17.14
	<hr/>
	100.00

I : Zn :: 1 : 2.4.

ZnO : H<sub>2</sub>O :: 1 : 1.8.

The excess of water above what would correspond to zinc oxide is evidently due to incomplete drying, as the substance cannot be heated to  $100^{\circ}$  without decomposition.

I would take this opportunity of expressing my cordial thanks to Professor Crum Brown and Dr. Leonard Dobbin for many important suggestions received during the investigation.

CHEMICAL LABORATORY,  
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## VARIATIONS IN THE COMPOSITION OF RED LEAD.<sup>1</sup>

BY DURAND WOODMAN.

IN the manufacture of red lead and orange mineral, the color is ordinarily the property of first importance, since its chief use is as a pigment; and except so far as the color is dependent on the degree of oxidation, the latter is not the subject of special consideration.

For certain purposes, however, the degree of oxidation is important, and having occasion to examine a large number of samples of red lead from various sources, I adopted the method of digesting in saturated solution of normal lead acetate, by which the litharge in excess of that in combination as  $\text{Pb}_3\text{O}_4$  (or  $2\text{PbO} \cdot \text{PbO}_2$ ) is dissolved out and separated. The samples were all examined qualitatively for anything which might be considered as adulteration, but otherwise neglecting the small amounts of silica, lime, oxide of iron, and carbon dioxide normal to the commercial article, for the preliminary and approximate tests. In this way a series of results was obtained showing a variation in the amount of actual red lead from 41 to 92 per cent., as given in the tabular statement.

No. or mark.	1.	2.	3.	4.	5.	6.	7.	8.	9.	10.
Red lead, $\text{Pb}_3\text{O}_4$ . . . .	51.0	56.0	72.0	75.0	41.0	90.0	89.5	70.0	87.0	89.5
Litharge, $\text{PbO}$ . . . . .	49.0	44.0	28.0	25.0	59.0	10.0	10.5	30.0	13.0	10.5

No. or mark.	517.	140.	C.	BWL.	C.	BWL.	C.	L. B.	BWL.	L. B.
Red lead, $\text{Pb}_3\text{O}_4$ . . . .	60.0	84.0	50.0	60.0	58.0	77.0	66.0	90.0	73.5	87.5 92.0
Litharge, $\text{PbO}$ . . . . .	40.0	16.0	50.0	40.0	42.0	23.0	34.0	10.0	26.6	12.5 8.0

The figures for red oxide are in most instances a little high because of the insoluble impurities which have not been determined and deducted, but the point which it is desired to bring out, is the large amount of monoxide in some samples,

<sup>1</sup>Read before the January meeting of the New York Section of the American Chemical Society.

which has escaped oxidation ; is separable by the lead acetate treatment ; and which I believe, from the ease with which it is so separated, has no part in the chemical constitution of red lead. It seems to be simply an admixture and a measure of the incompleteness and imperfection of the roasting or oxidizing process.

In this connection some interesting data are given in Gmelin's Handbook, Vol. v, p. 118, concerning the degree of oxidation corresponding to the length of time on the hearth of the reverberatory furnace in the roasting process.

"Red lead" prepared from massicot with

1 firing	of 24 hours,	contains 50.0 per cent. red lead ( $\text{Pb}_2\text{O}_3$ ).
2 firings	" " " "	52.1 " " " "
3 " "	" " " "	58.1 " " " "
4 " "	" " " "	64.1 " " " "
5 " "	" " " "	66.2 " " " "
8 " "	" " " "	74.8 " " " "

Red lead from "white lead" with 3 firings of 24 hours contained 95.3 per cent. red lead ( $\text{Pb}_2\text{O}_3$ ).

The analyses which I have made seem to show that little or no improvement has been made in the methods of manufacture from the standpoint of more complete oxidation.

The lead acetate treatment has a special interest in that it is one of the methods used by Dumas to demonstrate the individuality of the red oxide as a true chemical compound, although his results led him to the supposition that it was a sesquioxide [ $\text{Pb}_2\text{O}_3$ ] rather than a chemical union of the monoxide and peroxide.

The separation of the lead monoxide and red lead by this method is quite sharp, prolonged digestion in the acetate solution failing to produce any appreciable change in the weight of red lead.

By the usual methods of analysis, depending on the decomposition of the red lead into peroxide, which remains insoluble, and monoxide, which dissolves, no distinction is made between the monoxide in combination according to the formula  $2\text{PbO} \cdot \text{PbO}_2$ , and that which is present in excess and so easily removed by the acetate solution. An analysis of red lead is generally stated as follows :

	Per cent.
Peroxide, $\text{PbO}_2$ .....	26.4
Litharge, $\text{PbO}$ .....	69.7
Impurities.....	3.5
	<hr/> 99.6

Since the formula  $\text{Pb}_3\text{O}_4$  is accepted, and this compound is the essential part of a red lead, no matter what may be the views held as to whether the excess of  $\text{PbO}$  is a mere admixture, or in weak chemical combination; it would seem more satisfactory for commercial work to state an analysis as follows:

	Per cent.
Peroxide of lead, $\text{PbO}_2$ .....	26.4 per cent.
Equivalent to red lead.....	75.6
Lead monoxide (litharge) .....	20.5
Impurities .....	3.5
	<hr/> 99.6

If the acetate method is used, we obtain the red lead figure directly; if methods yielding the peroxide or its equivalent, the amount of peroxide found should be multiplied by the factor 2.866 to give the corresponding quantity of red lead.

#### DISCUSSION.

In regard to the lead monoxide removable by digestion of red lead in solution of lead acetate, Professor Sabin said that in making a cement of litharge and glycerine, considerable inert material, as sand or powdered glass, might be mixed with it without affecting the setting qualities; while on the contrary, red leads would not make a cement when mixed with glycerine. This would seem to indicate that the litharge is not in the same condition as if in simple admixture.

### SODIUM PEROXIDE AS A THIRD GROUP REAGENT.

BY S. W. PARR.

Received February 1, 1897.

**S**ODIUM peroxide as a reagent has properties of a very unusual and striking character. These properties are no less valuable than peculiar, and indicate for this substance a prominent place in analytical work. The immediate object of this paper is to note the advantages and adaptability of sodium peroxide to qualitative analysis. By this means its numerous characteristics can be best illustrated. The specific data indi-

cating its use in certain lines of quantitative analytical work will be given later. The methods herein set forth have been employed in this laboratory during the past year by large classes in qualitative analysis. This practical test of the processes involved has abundantly demonstrated their value.

In the ordinary procedure for the separation of the metals the greatest difficulty arises in the third or iron group. These complications may be briefly enumerated as follows :

(a) The separation of zinc in the presence of chromium.

(b) The unsatisfactory separation of cobalt and nickel from the other members of the group by the action of dilute hydrochloric acid on their sulphides.

(c) The variations arising from the presence of phosphates, etc.

It is not necessary to enlarge upon these difficulties. The one most commonly ignored in methods as usually outlined and yet a very serious obstacle, is the one designated under (a). Zinc and chromium enter into a combination which to a very large extent resists the action of ammonia and ammonium salts. The use of barium carbonate to obviate this difficulty is cumbersome. By use of sodium peroxide we may oxidize the chromic compounds present to sodium chromate, and thus completely eliminate it as a factor in any precipitation likely to be employed, excepting of course such as would involve a reduction and return to the condition of a chromic salt.

The method of procedure is as follows: The solution should be slightly acid. A small porcelain spoonful of the peroxide is slowly sifted in with constant stirring. The solution is then heated to complete the decomposition of the peroxide and finally boiled for some minutes after the oxygen seems to be all driven off. The completeness of the oxidation may be easily tested by filtering from any insoluble constituents, acidifying, boiling, and making ammoniacal. A precipitate may be aluminum or unoxidized chromium. Filter and wash free from all sodium chromate, redissolve in a little nitric acid and treat as before with a small amount of sodium peroxide. A yellow coloration is due to the chromium which escaped oxidation by the first treatment. However, if properly conducted, the first operation should be complete. Similarly, the insoluble residue on the filter, if suspected of being a zinc-chromium compound, may be

washed free from chromate, dissolved in dilute nitric acid, and treated again with the peroxide. The only condition so far governing the completeness of the transformation to the chromate form is the necessity of starting the oxidation with the chromium entirely in solution. Precipitated chromium hydroxide will undergo this transformation, but less readily, and especially if the precipitate is the double one of zinc and chromium. Hence the advisability of beginning the oxidation with the solution containing some free acid, preferably nitric. The quantity of free acid is immaterial, less than one cc. being sufficient. It should be noted, however, that the amount of sodium peroxide should cause the solution to pass quite beyond the neutral condition since the oxidation is only partial while in the acid state. It might be expected that the moment the addition of sodium peroxide passed the neutral point the precipitation of chromium would commence and the completeness of the oxidation be lessened in consequence, but I have not found this to be the case. The oxidizing action of the peroxide is so pronounced that it precedes the precipitating action, hence the reason for using the dry sodium peroxide. A cold saturated solution of the peroxide will operate but incompletely. Hydrogen peroxide will also act similarly, but even less completely than the solution of sodium peroxide. For obvious reasons also the operation is performed on the solution before heating, and it is better to shake the powder in gradually than to drop the reagent in at once.

We are ready now to note the effect of such treatment as above indicated, upon the other members of this group, assuming that any or all may be present, including cobalt and nickel. The results are as follows :

(a) Aluminum compounds are in solution in the form of sodium aluminate, not different from the ordinary result from using sodium hydroxide in excess. It is assumed of course that the sodium peroxide has exceeded the free acid in sufficient amount to provide sodium hydroxide in excess.

(b) Zinc is similarly in solution as zincate.

(c) Iron precipitates as a very dense, reddish-brown precipitate, the exact composition of which is being made a matter of investigation. The precipitation is complete, no re-solution being effected upon boiling. The filtration is performed with great

facility. The precipitate is almost insoluble in concentrated nitric acid; soluble in dilute acids on heating. If phosphates are present, none are precipitated with the iron, but all pass through and are found in the filtrate.

(*d*) Manganese behaves exactly as iron, precipitating presumably as the hydrated dioxide,  $\text{MnO}_2 \cdot x\text{H}_2\text{O}$ , having all the properties of that compound as to color, solubilities, etc. Similarly also, phosphates are not precipitated. It should also be noted that from this precipitate can most readily be obtained the delicate test for the presence of manganese by formation of permanganic acid by means of nitric acid and lead peroxide or  $\text{Pb}_2\text{O}_3$ .

(*c*) Cobalt precipitates also a black hydrated cobaltic oxide with solubilities the same as in the case of iron and manganese. No phosphate is precipitated with the cobalt. The precipitate, in conjunction with dilute acid and potassium iodide, liberates free iodine, imparting an intense blue to starch solution. This latter property, however, is common to the precipitates of iron and manganese under (*c*) and (*d*).

(*f*) Nickel precipitates, as the ordinary green nickelous hydroxide,  $\text{Ni}(\text{OH})_2$ , easily soluble in acid, either concentrated or dilute. As to phosphates, in the case of nickel, if present in large amounts, small quantities are found in the precipitated nickel. A re-solution and reprecipitation with sodium peroxide, however, eliminates all the phosphate from the precipitate. The behavior of nickel in thus precipitating as the nickelous compound indicates for its higher form of oxidation a less degree of stability than exists in the case of cobalt. This property suggests the readiest and most delicate method for the detection of nickel, even in the presence of the three precipitates enumerated above, thus: boiling this precipitate of nickel with bromine water converts it at once into the black nickelic hydroxide, which has the property of decomposing potassium iodide with water alone, no acid being required, as in the case of iron, manganese, and cobalt. It is necessary, of course, to boil off the free bromine, which is readily accomplished. The action upon a potassium iodide starch solution is very marked.

The above facts suggest a method for the iron group which is



indicated by the following table. It is given here to illustrate the adaptability of some of the well-known but more positive and satisfactory tests for the several metals.

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The precipitate obtained in the ordinary method by means of ammonium hydroxide and ammonium sulphide contains, as hydroxides and sulphides, iron, manganese, cobalt, nickel, aluminum, zinc, and chromium, and is brought into solution by means of ten to fifteen cc. of concentrated nitric acid with heat. Nearly neutralize with sodium hydroxide, then sift in slowly with stirring sodium peroxide in excess. Boil.

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Precipitate A contains iron, manganese, cobalt, and nickel.

(a) Test for iron by dissolving a small portion of the precipitate in dilute hydrochloric acid and adding potassium thiocyanate. The blood red coloration is due to ferric thiocyanate.

(b) For manganese, to five cc. water add five cc. concentrated nitric acid and five to ten grams  $Pb_3O_4$ . Stir into the warm mixture a little of the precipitate and let stand. A purple solution is permanganic acid.

(c) In absence of iron or manganese, stir a little of the precipitate into dilute hydrochloric acid and add solution of potassium iodide and starch. In presence of iron and manganese use the bead test.

(d) Boil some of the precipitate with bromine water till all bromine is expelled, add water and solution of potassium iodide and starch,  $Ni(OH)_2 + KI = Ni(OH)_2 + KOH + I$ , imparting the blue to the solution.

Solution A contains all the aluminum, zinc, and chromium. The yellow color is evidence of chromium. Acidify with hydrochloric acid, boil, and add ammonium hydroxide.

Precipitate B consists of aluminum hydroxide, and any chromium hydroxide that may have escaped oxidation. Dissolve in nitric acid and repeat the precipitation with sodium peroxide, or apply the blowpipe and cobalt test for aluminum.

Solution B contains zinc and chromium.

(a) Test for zinc by adding to a portion a few drops of potassium ferrocyanide. A heavy white precipitate indicates zinc.

(b) If further verification of chromium is needed, make the solution acid with hydrochloric acid and boil with a little alcohol added. The chromium reverts to the green chromic chloride.

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In the presence of phosphates the method so far employed has been as follows: Upon dissolving the precipitate from the ammonium sulphide in concentrated nitric acid a very little of the solution is tested for phosphoric acid in the usual manner. If

present, granulated tin is added and the boiling continued. Filter from the insoluble tin phosphate, make ammoniacal, reprecipitate with ammonium sulphide, and proceed as with phosphoric acid absent. Any method not involving the use of tin and depending upon the non-formation of the phosphates of iron, manganese, and nickel, is as yet unsatisfactory. Having removed the barium and strontium with sulphuric acid before the precipitation with ammonium sulphide, the oxidation and precipitation by means of sodium peroxide may be performed as usual, but before filtering, the solution is made acid with acetic acid and boiled a little further and filtered. The filtrate now may contain besides the aluminum, zinc, and chromium, the nickel which is readily soluble in acetic acid, and the calcium and magnesium which has been brought along by means of the phosphoric acid. A little of the cobalt, however, dissolves with the acetic acid and a solvent has not been found thus far for the calcium phosphate and nickel hydroxide that will not dissolve traces of the other three metals of the precipitate.

One other application to qualitative analysis may be mentioned as having proved valuable. In testing for acids a ready method for distinguishing between carbon dioxide and sulphur dioxide when both are present is found in the use of a solution of sodium peroxide. Conducted into this solution, the above gases form sodium carbonate and sodium sulphate respectively. With lime-water the solution will give a copious precipitate if the carbonate has been formed, and with an acidulated solution of barium chloride the sulphate test is obtained.

Many other features incidental to the properties above outlined have developed, mainly of interest in quantitative methods. It is hoped that the data will be of sufficient value to warrant further notice.

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[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF PURDUE  
UNIVERSITY.]

## THE QUANTITATIVE DETERMINATION OF CARBOHY- DRATES IN FOOD STUFFS, II.

BY W. E. STONE.

Received March 24, 1897.

IN a preceding number of this Journal a plea was made for a more definite knowledge of the constituents of the "nitrogen-free extract" of food stuffs, and a method of analysis was proposed for differentiating between the various carbohydrates included in that term.

The analytical data there presented were in part obtained in an investigation upon the carbohydrates of wheat and maize, done by the writer and published as Bulletin 34 of the Office of Experiment Stations, U. S. Department of Agriculture. This method of estimating carbohydrates was employed there for the first time, and was necessarily imperfect in some of its details. This was notable in the starch determinations, which gave results much too low. This error was noticed by the author, but too late to be corrected in the original paper. It was corrected, however, in the article referred to in the March number of this Journal, in which the scheme for analysis was first described in detail. The error consisted in the employment of too dilute acid for the hydrolysis of the starch products, previously rendered soluble by the action of malt extract upon the material under examination. Originally one cc. of concentrated hydrochloric acid to 100 cc. of the solution under treatment was employed. As modified on pp. 188-189 of the March number of this Journal, ten cc. of concentrated hydrochloric acid are added to 100 cc. of the solution and the whole heated for one hour in boiling water. This correction was made as the result of a comparative study of the strength of acid and duration of treatment necessary to completely change diastatic starch products into dextrose. At the time of going to print, the writer had been unable to complete the treatment of all the materials under investigation, according to this revision. The original starch data obtained with more dilute acid, were therefore presented and attention was called to their derivation on p. 193.

It is now possible to present the results obtained from the

original samples, using the corrected method of hydrolysis described on pp. 188-189, as follows :

NORMAL STARCH DISSOLVED BY MALT EXTRACT.

	Per cent.
Wheat I.....	57.62
Wheat II.....	56.27
Wheat flour I.....	67.99
Wheat flour II.....	67.76
Maize .....	65.45
Bread from Wheat I .....	53.54
Bread from Wheat II.....	53.62
Bread from Flour I.....	64.81
Bread from Flour II.....	64.12
Bread from Maize.....	61.64

It will be noted that the amounts of starch have been increased from fifteen to twenty per cent. over those originally given.

In the previous paper it is said, " In many cases it is believed that the total amount of carbohydrates thus definitely determined in food materials, will be found to be appreciably less than the nitrogen-free extract estimated by difference." This discrepancy, amounting to twenty or thirty per cent., as based upon the earlier and erroneous starch determinations, is diminished by the later results, but still exists to an extent which cannot be overlooked, as will appear from the following summary :

RESPECTIVE PERCENTAGES OF DIFFERENT CARBOHYDRATES IN DIFFERENT FOOD STUFFS.

	Sucrose.	Invert sugar.	Dextrin.	Soluble starch	Normal starch	Pentosans.	Crude fiber.	Total.	Nitrogen-free extract.
Wheat I.....	0.52	0.08	0.27	0.00	57.62	4.54	2.68	65.71	77.07
Wheat II .....	0.72	0.00	0.41	0.00	56.27	4.37	2.51	64.28	77.66
Flour I .....	0.18	0.00	0.90	0.00	67.99	0.00	0.25	69.32	83.54
Flour II.....	0.20	0.00	1.06	0.00	67.76	0.00	0.25	69.27	84.54
Maize .....	0.27	0.00	0.32	0.00	65.45	5.14	1.99	73.17	78.02
Bread (Wheat I) ..	0.14	0.10	0.68	1.37	53.54	4.16	2.70	62.59	77.20
Bread (Wheat II) ..	0.05	0.32	0.23	2.36	53.62	4.34	2.42	63.34	77.33
Bread (Flour I) ...	0.06	0.37	0.27	1.99	64.81	0.00	0.34	67.84	82.94
Bread (Flour II) ..	0.15	0.38	0.91	1.74	64.12	0.00	0.17	67.47	85.17
Corn bread (Maize)	0.16	0.19	0.00	2.80	61.74	3.54	2.22	70.75	77.81

This discrepancy may arise from one of two sources; viz., 1.

Error in the determination of carbohydrates. 2. The existence of a substance which is free of nitrogen and is of a character not usually ascribed to carbohydrates and resistant to the ordinary reactions for such. While the first alternative is not excluded, the writer is inclined to the latter conclusion and expects to continue the investigation along this line.

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### NOTE.

*Improvement in Drying Chambers.*—In an ordinary copper drying chamber, or air-bath, the bottom is protected by a false bottom, usually of iron, supported at the four corners by the legs of the chamber. When heated by a burner the false bottom expands and cups, and thus breaks the heat connection with the true bottom, making the chamber more difficult to heat. This trouble may be entirely remedied by riveting the two bottoms in the center with one rivet, leaving the four corners to expand or contract, but still supported by the legs of the chamber. The burner should be placed immediately under the rivet. The writer has used chambers thus improved for some time with great satisfaction. Chambers with the improved bottom may be had of Eimer & Amend, New York. J. L. BEESON.

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### NEW BOOKS.

**THE ENERGY OF LIVING PROTOPLASM.** By OSCAR LOEW. Professor in the Imperial University, Japan. 1896. London: Kegan Paul, Trench, Trübner & Co.

After reviewing briefly the theories of the cause of vital phenomena held from the time of Plato to the present, and after giving a short history of the discovery of the cell, the author takes up the characteristics of protoplasm, and especially those by which this substance exhibits phenomena of sensation. This naturally leads to a discussion of the relations of proteids to protoplasm, and consequently to a sharp distinction between physiologically active and dead or reserve proteid matter. He considers that proteids yield the vital phenomena, and that living proteid matter undergoes a chemical change at the moment of death. After briefly reviewing the older theories respecting the constitution of the proteid molecule he concludes with the following: "It appeared to me that more insight into the chemical nature of the proteids

could be obtained by the study of the *formation of proteids in plant cells*. Starting from a series of observations I reached a hypothesis which led me to infer the existences of a labile and stable modification of albumin, as explaining in a more satisfactory manner than the views of Pflüger and of Latham the difference between the proteids of living protoplasm and those of dead."

To get a clew to the formation of proteids he studied the nutrition of lower fungi and phaenogams. Microbes are especially characterized by their great chemical activity—one cell under favorable conditions multiplying in twenty-four hours to more than a trillion new cells. In this process the complex organic substances which serve as food are broken down, and by synthetic processes the protoplasm and other constituents of the plant cells are created. Although different chemical bodies serve as nourishment the same proteids are formed, for otherwise new species would result. He has found that the same species persists whether fed on glycerol, glucose, galactose, acetic or quinic acid; or whether leucin, betain, asparagin or kreatin furnish nitrogen.

From this it must be concluded that proteids are formed from substances so simple that they may be derived from each of these widely differing bodies. Since the simplest compounds which can be utilized by plants for the formation of proteids are methyl alcohol, methylamine, and methyl sulphuric acid, the "starting group must contain only one atom of carbon in the molecule."

"Since methyl alcohol and methylamine as such do not serve for synthetic operations, transformation into a compound capable of condensation must take place, and this can only be formaldehyde, the same substance that forms, by condensation, various kinds of sugars."

Formaldehyde is a poison, but owing to the extreme ease with which it is condensed, and to the fact that certain compounds of this aldehyde are quite harmless, this objection has no great weight, for no molecule remains unchanged for a second.

*Bacillus methylicus*, a species of microbe, can derive its entire organic nutriment from the acid sodium sulphite compound of formaldehyde as well as the compound of formaldehyde with ammonia. In the case of the nitrifying microbe, which can utilize ammonium carbonate, it is probable that formaldehyde

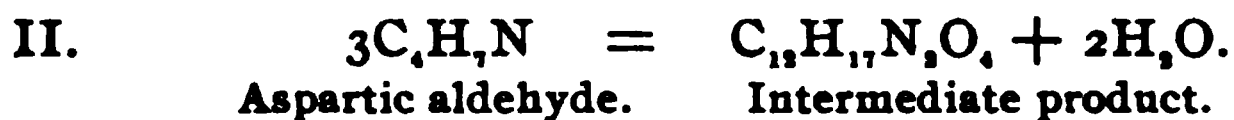
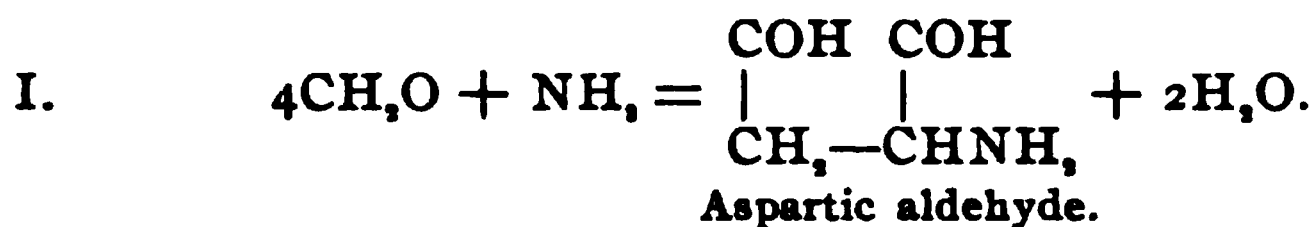
results from the carbon dioxide through the aid of the hydrogen of the ammonia.

By a similar line of reasoning Loew concludes that ammonia serves as the simplest source of nitrogen.

In regard to sulphur, there is little doubt that this is present in the proteid molecule in a reduced state and consequently sulphur compounds must be reduced to hydrogen sulphide in proteid formation. We may therefore infer that the atomic groups necessary for the formation of the proteid molecule are formaldehyde, ammonia, and hydrogen sulphide.

After discussing the relations of asparagin to proteid formation and decomposition, which has been so many times pointed out by numerous observers, he asks: "How can we explain the transformation of asparagin into albumin?" Asparagin, being a relatively simple compound, while albumin is one of the most complex, the latter must be derived from the former by some transformation which can readily take place. Such a process would be possible if aspartic aldehyde were formed and subsequently condensed.

The formation of albumin from formaldehyde and ammonia he represents as taking place according to this theory in the following way:



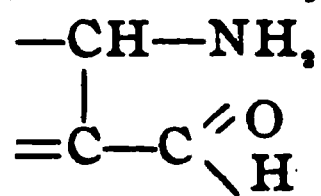
For II it is assumed that condensation proceeds between the aldehyde and methylene groups, while in equation III condensation occurs after the type of pinacone formation, a highly unstable substance resulting, containing twelve aldehyde and eighteen amido groups, which possesses much kinetic energy in the form of motions of the labile atoms.

By atomic migration it would, with the loss of aldehyde characters, become a relatively stable substance, the ordinary albumin.

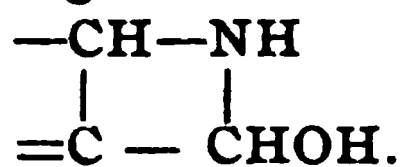
As evidence of the existence in the living cell of a peculiar active form of proteid, he describes an "active albumin" whose presence in a large number of plants was revealed by the action of dilute solutions of organic bases.

This form of albumin differs from passive albumin by a greater power of holding water in combination; by forming insoluble compounds with certain organic bases; by being coagulated with very dilute alcohol, ether vapor, and dilute prussic acid; and by reducing highly dilute silver solutions.

These differences from passive albumin are ascribed to the existence of active aldehyde groups in the molecule of the active albumin, which by atomic migration become converted into passive groups, as shown by the following formula:



Active.



Passive.

The source of energy of living cells he ascribes to the kinetic energy of labile atoms within the proteid molecule and as evidence of this he compares the properties of living protoplasm with labile organic compounds, which are easily changed by heat, acids, or alkalies into stable, isomeric, or polymeric products, whereby contraction takes place and heat is developed. These labile bodies can cause chemical changes in other compounds, those containing labile hydrogen atoms having an especial affinity for oxygen.

Loew's theory of the formation of albumin supplies this necessary labile condition of protoplasm through the proximity of aldehyde and amido groups, for amido aldehydes have recently been shown to be very labile substances. As evidence of the existence of such groups in protoplasm the poisonous effect of substances readily reacting with aldehydes and amides is discussed at length. As aldehydes and amides react upon one another the danger of self-poisoning of protoplasm becomes great, a condition which the author considers as occurring when protoplasm is heated above 50°, its contained albumin being thereby changed from the active to the passive state in the manner indicated in the formula last given.

Coming next to a discussion of the chemical activity of the



living cell he finds the cause of this in the katalytic power of the protoplasm, which power is due to the oscillating motion of the labile atoms of the proteid constituents. It is by means of the energy imparted by these labile atoms that the oxidations occurring in respiration take place and thus this appears as the source of the energy of living protoplasm.

Whatever views the reader may hold respecting this theory and the evidence on which it rests he cannot fail to find much food for thought in the multitude of facts brought together in this volume. The book abounds in references so that a practically complete bibliography of the subject is given, a fact which alone gives the work much value.

THOMAS B. OSBORNE.

TABLES FOR THE DETERMINATION OF MINERALS BY PHYSICAL PROPERTIES, BASED ON THE SYSTEM OF DR. A. WEISBACH. BY PERSIFOR FRAZER. Fourth Edition. pp. 163. Philadelphia: J. B. Lippincott Co. 1897. Price \$1.50.

These tables are well printed, the arrangement clear, the various physical properties succinctly, yet accurately, enumerated, and the remarks on blowpipe reactions and associated minerals very well written. There is an unfortunate confusion in the use of the term "*sectile*," which as defined by Dana and used by accurate mineralogists, means that the substance can be sliced into shavings with a knife, but goes to pieces on hammering. Dr. Frazer uses *sectile* in place of Weisbach's *weich*, which is very clearly used as meaning simply *soft*; and again uses the same word in place of the German *mild*, which as used by Weisbach means that the substance is not brittle, but cuts like white china clay or stibnite. The result of this confusion is that the tables sometimes classify a mineral as *sectile* in one sense, but not *sectile* in another sense; while the same mineral is not *sectile* at all according to the definition of Dana!

It would have been far better to have used *soft* in the first case and *mild* in the second, explaining the meaning that word has when applied to minerals, while *sectile* could be reserved for its exact use according to definition.

Aside from these commendations and criticisms, and while acknowledging the tables the best of their kind, the reviewer must record his opinion that "*the kind*" is not the best one. Mineral

tables based on "physical properties" are radically wrong in principle. Dr. Frazer himself emphasizes in italics the truth that "*Every true mineral is a definite chemical compound or element*," and it thence follows that every true scheme of determining minerals should start and be based on their *chemical composition*, bringing in physical tests *afterwards* to verify the chemical determination, or to distinguish between the few minerals which contain the same ingredients or respond to the same tests. The Weisbach method starts at the wrong end, and while it may and does give to beginners a superficial acquaintance which enables them to identify the *usual* forms of the *common* minerals, yet it is totally unfit to guide in the accurate determination of minerals in general.

JOSEPH W. RICHARDS.

PHYSICAL LABORATORY MANUAL FOR SECONDARY SCHOOLS. BY CHARLES F. ADAMS, A.M., Teacher of Physics in Detroit Central High School. 12 mo. pp. 184. 1896. New York and Chicago: Werner School Book Company. Price, 75 cents.

While the number of elementary manuals for physical laboratory instruction continues to increase, it is rare to observe among them any decided advance either in methods or plan. In the book before us the author has sought to eliminate qualitative exercises "or illustrative experiments," as he calls them, and to confine the pupil's attention to comparatively few exercises, the greater part of them being quantitative in character. It would seem, however, that, especially in elementary instruction, there is a proper place for qualitative physics as there certainly is for qualitative chemistry. Indeed, in certain parts of the subject, as, for instance, in physical optics and in electrostatics, qualitative experiments are an almost necessary preparation for quantitative ones. A judicious combination of the facts of physics, ascertained by qualitative experiments, with the laws of physics, proved and verified quantitatively, would seem to constitute the best basis for an elementary laboratory text-book. While there is not much that is novel in Mr. Adams' text-book it is well arranged, the experiments are for the most part well chosen, and the descriptions are clear and concise. The emphasis with which care in entering the results in the note-book is insisted on, is particularly to be commended.

G. F. BARKER.

**LABORATORY CALCULATIONS AND SPECIFIC GRAVITY TABLES.** BY JOHN S. ADRIANCE, A.M. Third Edition. Revised and Enlarged. 1897. ix + 144 pp. Price, \$1.25.

This little book, which is well known to many chemists, appears in a new and somewhat enlarged edition.

Many an analyst has felt impatient at the loss of time necessary in making analytical calculations. To such this book will be found useful, containing as it does calculations for most of the reagents employed in analytical chemistry. The percentage and specific gravity tables, which are numerous, as well as the directions for preparing many reagents, will be found convenient.

It is to be regretted that the atomic weights employed by the author could not have been taken from the recent edition of Professor Clarke's "Constants of Nature," instead of his tables published in 1882. The book as it is, however, will be useful to most chemists, and should find a place in every well regulated laboratory.

J. F. MCGREGORY.

**AN INTRODUCTORY COURSE OF QUANTITATIVE CHEMICAL ANALYSIS, WITH EXPLANATORY NOTES AND STOICHIOMETRICAL PROBLEMS.** BY HENRY P. TALBOT, PH.D., Associate Professor of Analytical Chemistry in the Massachusetts Institute of Technology. 125 pp. New York: The Macmillan Co. Price \$1.50.

There are few readers of analytical chemistry who have not felt the need of a book which shall in a clear and concise style give the principles of quantitative analysis, and sufficient of the practice to enable the student to make his way in the larger and fuller manuals. Such a book is needed not only for those who expect to become analytical chemists, but for the much larger number who pursue chemistry in colleges, merely in course of a general education. It is hardly too much to say that it is difficult to see how a better book could be prepared for this purpose than the one before us. The general directions and the specific directions under each analysis are so clearly given that an instructor could oversee the work of a large number of students, and in each case the theory of every step is so lucidly explained that the book has a distinct educational value. The examples are well chosen and illustrate the most important methods of procedure. They are in gravimetric analysis, chlorine, iron, sulphuric acid, phosphorus pentoxide, calcium and magnesium in dolomite, lead, copper (electrolytic), and zinc in

brass ; in volumetric analysis, calibration, preparation of half-normal hydrochloric acid and sodium hydroxide, soda ash, oxalic acid, iron (bichromate), chromium in chrome iron ore, iron (permanganate), pyrolusite, iodimetry, antimony in stibnite, bleaching powder, and silver (potassium thiocyanate).

The book closes with a very useful chapter on stoichiometry, containing typical problems, and a table of four place logarithms.

JAS. LEWIS HOWE.

TRAITÉ ÉLÉMENTAIRE DE CHIMIE. PAR. A. HALLER, Correspondant de l'Institut, Directeur de l'Institut Chimique de la Faculté des Sciences de Nancy, et P. Th. Muller, Maître de Conférences à l'Institut Chimique de la Faculté des Sciences de Nancy. Paris: Carré et Naud.

This work appears in two octavo volumes, the first of 336 pages, being devoted to inorganic chemistry, and the second, of 205 pages, to organic. It is a brief outline of general chemistry and presents nothing essentially new. Nevertheless, as an outline it is very complete, dealing with the entire subject in a clear and satisfactory manner, and including many topics which are usually discussed in larger text-books only. As an illustration of its scope it may be mentioned that attention is given to such subjects as argon, carborundum, and nickel carbonyl. In the volume upon organic chemistry the new nomenclature of carbon compounds is used, but this part of the work would be of greater interest to students if a systematic discussion of nomenclature were introduced. To American readers who wish to gain a knowledge of scientific French this work can be recommended. A chapter (19 pages) devoted to qualitative analysis will still further increase its value considered as a sort of introduction to French chemical literature.

FRANCIS C. PHILLIPS.

NOTES ON ASSAYING. BY PIERRE DE PEYSTER RICKETTS, E.M., PH.D. AND EDMUND H. MILLER, A.M., PH.D. viii + 311 pp. New York: John Wiley & Sons. Price, \$3.00.

The best part of this book is the part that does not treat of assaying ; *viz.*, Parts III, IV, and V. These are devoted to chemical analyses, both quantitative and qualitative, blowpipe tests, laboratory extraction tests, and the usual tables, together with some new ones. Among the latter are tables of the characteristics of ores and of metals, and a table of solubilities. These features are good ones and make any laboratory handbook convenient and valuable.

Parts I and II, devoted to apparatus, reagents, and schemes for fire assays, contain so much useless and misleading information that the valuable portion is lost completely to the inexperienced reader. It would have been much better had the authors reduced these one hundred and thirty-nine pages to thirty.

**HANDBOOK FOR THE BIO-CHEMICAL LABORATORY, INCLUDING METHODS OF PREPARATION AND NUMEROUS TESTS ARRANGED ALPHABETICALLY.** BY JOHN A. MANDEL. New York: John Wiley & Sons. pp. 101. Price, \$1.50.

In this little book the author presents a very good compilation of laboratory processes for the production of a number of substances of physiological importance. Many of the descriptions of methods appear to be taken from well-known books of Drechsel, Halliburton, Gamgee, and others, but a distinct service has been rendered American students by bringing them together in compact form. Most of the processes described have stood the test of student practice and can be recommended as workable.

A list of common tests, employed mostly in laboratories of physiological chemistry, takes up about thirty-five pages of the book. Some of these tests are good, others could have been omitted without lessening the value of the book, as they are practically useless in investigation. In this part of the book several typographical errors have escaped the notice of the author. On page 76, for instance, "liquor of potassæ" should not have been overlooked, and on page 85, under the Molisch test "solution of a naphthol" should read "solution of  $\alpha$ -naphthol." Other errors noticed are of minor importance and not misleading.

J. H. LONG.

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### BOOKS RECEIVED.

**Tables for the Determination of Minerals by Physical Properties.** By Persifor Frazer. xii + 163 pp. J. B. Lippincott Co. 1897. Price, \$1.50.

**The Woolly-Aphis of the Apple.** Bulletin No. 35. Agricultural Experiment Station of the State of Missouri. Columbia, Missouri. July, 1896. 26 pp.

**An Introductory Course of Qualitative Chemical Analysis with Explanatory Notes and Stoichiometrical Problems.** By Henry P. Talbot, Ph.D. 125 pp. 1897. New York: The Macmillan Co. Price, \$1.50.

**Some Notes Concerning the Nitrogen Content of Soils and Humus.** By Elton Fulmer. Bulletin 23. Washington State Agricultural College and School of Science. Pullman, Washington, October, 1896. 19 pp.

**Experiments in the Culture of the Sugar Beet in Washington for 1895 and 1896.** By Elton Fulmer. Bulletin 26. Washington State Agricultural College and School of Science. Olympia, Washington. December, 1896. 36 pp.

**The Phase Rule.** By W. D. Bancroft. 255 pp. Ithaca, N. Y.: Journal of Physical Chemistry. Price, \$3.00.

**The Chemistry of Dairying.** By Harry Snyder, B.S. viii + 156 pp. Easton, Pa.: Chemical Publishing Co. 1897. Price, \$1.50.

**Studies in Chemical Dynamics.** By J. H. van 't Hoff. vi + 286 pp. 1896. Easton, Pa.: Chemical Publishing Co. Price, \$2.50.

**Engineering Chemistry.** By Thomas B. Stillman, M.Sc., Ph.D. With 154 illustrations. xxiv + 523 pp. Easton, Pa.: Chemical Publishing Co. 1897. Price, \$4.50.

**Principles and Practice of Agricultural Analysis.** By H. W. Wiley, Chief Chemist U. S. Dept. of Agriculture. Vol. III. Agricultural Products. xii + 666 pp. Easton, Pa.: Chemical Publishing Co. 1897. Price, \$3.75.

**Corn, Cotton, and Forage Plants.** Bulletin No. 40. Texas Agricultural College, College Station, Brazos Co., Texas. September, 1896. 24 pp.

**A Clinical Report on the Chemical Examination of Two Hundred Cases of Human Breast Milk.** By Vanderpoel Adriance, M.D., and John S. Adriance, A.M., F.C.S. 42 pp.

**Thirty-Fourth Annual Report of the Massachusetts Agricultural College.** Public Document No. 31. January, 1897. 356 pp. Boston: Wright & Potter Printing Co. 1897.

**Experiments with Corn and Crimson Clover, and Growing Cattle Without Coarse Feed.** Bulletin No. 46. January, 1897. 24 pp. University of Illinois, Agricultural Experiment Station, Urbana, Ill.

**Dairy and Food Laws of Wisconsin for the Years 1895-1896.** H. C. Adams, Commissioner. 315 pp. Madison, Wisconsin. Democrat Printing Company, State Printers.

**Digest of Criticisms on the United States Pharmacopœia, Seventh Decennial Revision (1890).** Part I, comprising abstracts of paper to July 1, 1896. 183 pp. Published by The Committee of Revision and Publication of the Pharmacopœia of the United States of America (1890-1900).

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The paper on "The Distribution of the Precious Metals in Copper," by Edward Keller, printed in the March issue of this Journal, was presented at the February meeting of the American Institute of Mining Engineers. Mention of this fact should have been made.

# THE JOURNAL

OF THE

## AMERICAN CHEMICAL SOCIETY.

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### FOURTH ANNUAL REPORT OF THE COMMITTEE ON ATOMIC WEIGHTS. RESULTS PUBLISHED IN 1896.

BY F. W. CLARKE.

Received January 8, 1897.

*To the Members of the American Chemical Society :*

**D**URING 1896 the activity in the determination of atomic weights was only moderate. Comparatively few papers on the subject appeared, but some of these were of excellent quality. The question is often asked, Why are new determinations important? Are not those we have good enough for all practical purposes? To this question I have an interesting answer, such as has not hitherto been published.

There are two rival values for the atomic weight of chromium. One, 52.5 approximately, based on the old work of Berlin, is still used by European analysts. The other, 52.1, depends upon later and more accurate researches, and is used in this country. Mr. William Glenn, of the Baltimore Chrome Works, informs me that that establishment imports chrome iron ore by the shipload, the value being determined by a volumetric assay in which the atomic weight of chromium is involved. It is assayed in Glasgow, with the older value for chromium, and in Baltimore with the modern datum. A cargo amounts to about 3500 tons; and the difference in price due to the difference between 52.1 and 52.5 for chromium, amounts to about \$367.50 per shipload. This difference is large enough to show the importance of accurately determined constants from a commercial point of view, and suggests that other similar cases might be found by a careful scrutiny of our analytical processes.

The following new determinations of atomic weights represent the work published during the year :

*Oxygen*.—In the report for 1895, J. Thomsen's gravimetric measurements of the H : O ratio were cited. Early in 1896 the same chemist,<sup>1</sup> by a novel method, determined the ratio of densities. First, he found the volume of hydrogen in liters, liberated by the solution of one gram of aluminum, to be as follows :

1.24297  
1.24303  
1.24286  
1.24271  
1.24283  
1.24260  
1.24314  
1.24294

Mean, 1.24289  $\pm$  0.00004

In his earlier research Thomson found the weight of hydrogen corresponding to one gram of aluminum to be 0.11190  $\pm$  0.000015 gram. Hence one liter of hydrogen at 0°, 760 mm., and 10.6 meters above sea-level is 0.090032  $\pm$  0.00012 gram; or at sea-level in latitude 45°, 0.089947.

For the volume of one gram of oxygen at 0°, 760 mm., and at Copenhagen Thomsen found, in liters :

0.69902  
0.69923  
0.69912  
0.69917  
0.69903  
0.69900  
0.69901  
0.69921  
0.69901  
0.69922

Mean, 0.69910  $\pm$  0.00002

At sea-level, latitude 45°, 0.69976  $\pm$  0.00002.

Hence one liter weighs 1.42906  $\pm$  0.00004 gram. Dividing this by the value found for hydrogen we have for the ratio desired

15.8878  $\pm$  0.0022.

<sup>1</sup> *Ztschr. anorg. Chem.*, 12, 4.



Correcting this by the known data for the volumetric composition of water we get

$$O = 15.8690 \pm 0.0022,$$

a value identical with that found gravimetrically, and very close to the measurement by Morley.

*Silver.*—The atomic weight of silver has been determined electrolytically by Hardin.<sup>1</sup> The nitrate, acetate, and benzoate, mixed in aqueous solution with solutions of pure potassium cyanide, were electrolyzed in platinum dishes. The data are as follows, with vacuum weights, and reduced with  $N = 14.04$ ,  $C = 12.01$ ,  $H = 1.008$ , and  $O = 16$ .

## NITRATE SERIES.

Weight $AgNO_3$ .	Weight Ag.	Atomic weight Ag.
0.31202	0.19812	107.914
0.47832	0.30370	107.900
0.56742	0.36030	107.923
0.57728	0.36655	107.914
0.69409	0.44075	107.935
0.86367	0.54843	107.932
0.86811	0.55130	107.960
0.93716	0.59508	107.924
1.06170	0.67412	107.907
1.19849	0.76104	107.932

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Mean, 107.924

## ACETATE SERIES.

Weight salt.	Weight Ag.	Atomic weight Ag.
0.32470	0.20987	107.904
0.40566	0.26223	107.949
0.52736	0.34086	107.913
0.60300	0.38976	107.921
0.67235	0.43455	107.896
0.72452	0.46830	107.916
0.78232	0.50563	107.898
0.79804	0.51590	107.963
0.92101	0.59532	107.925
1.02495	0.66250	107.923

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Mean, 107.922

<sup>1</sup> This Journal, 18, 990.

## BENZOATE SERIES.

Weight salt.	Weight Ag.	Atomic weight Ag.
0.40858	0.19255	107.947
0.46674	0.21999	107.976
0.48419	0.22815	107.918
0.62432	0.29418	107.918
0.66496	0.31340	107.964
0.75853	0.35745	107.935
0.76918	0.36247	107.936
0.81254	0.38286	107.914
0.95673	0.45079	107.908
1.00840	0.47526	107.962
		Mean, 107.938

The mean of all three series is

$$\text{Ag} = 107.928.$$

This value agrees well with the values found by Stas and by Marignac, and so creates a presumption in favor of the electrolytic method, which Hardin has also applied to determining the atomic weights of mercury and cadmium.

*Nitrogen.*—Among the ratios measured by Penny and by Stas relative to the atomic weights of nitrogen, those connecting the chlorides and nitrates of potassium and sodium were highly important. These are now redetermined by Hibbs<sup>1</sup> in a different way. The nitrates were heated in gaseous hydrochloric acid, and so converted easily into chlorides, with considerable accuracy. The data are as follows, with vacuum weights, and reduced with  $\text{O} = 16$ ,  $\text{K} = 39.11$ ,  $\text{Na} = 23.05$ , and  $\text{Cl} = 35.45$ .

Weight $\text{KNO}_3$ .	Weight $\text{KCl}$ .	Atomic weight N.
0.11090	0.08177	14.011
0.14871	0.10965	14.010
0.21067	0.15523	14.013
0.23360	0.17223	14.011
0.24284	0.17903	14.014
		Mean, 14.0118
Weight $\text{NaNO}_3$ .	Weight $\text{NaCl}$ .	Atomic weight N.
0.01550	0.01066	14.011
0.20976	0.14426	14.011
0.26229	0.18038	14.014
0.66645	0.45829	14.014
0.93718	0.64456	14.008
		Mean, 14.0116

<sup>1</sup> Doctoral Dissertation, University of Pennsylvania, 1896, by J. G. Hibbs. This Journal, 18, 1044.

These results seem to be exceedingly good, and the process has the advantage of great simplicity. The work was done under the direction of Prof. E. F. Smith.

*Arsenic.*—In the dissertation already cited Hibbs gives some determinations of the atomic weight of arsenic. Sodium pyroarsenate was heated in gaseous hydrochloric acid and so converted into chloride. The latter was perfectly white, unfused, and showed no trace of arsenic. I subjoin the vacuum weights, and the values found for arsenic when  $O = 16$ ,  $Na = 23.05$ , and  $Cl = 35.45$ .

Weight $Na_4As_2O_7$ .	Weight $NaCl$ .	Atomic weight $As$ .
0.02177	0.01439	74.904
0.04713	0.03115	74.921
0.05795	0.03830	74.927
0.40801	0.26981	74.901
0.50466	0.33345	74.916
0.77538	0.51249	74.917
0.82897	0.54791	74.917
1.19124	0.78731	74.926
1.67545	1.10732	74.928
3.22637	2.13267	74.901
		Mean, 74.9158

*Magnesium.*—Atomic weight determined by Richards and Parker,<sup>1</sup> who studied the carefully purified chloride. First, a gravimetric series, with all weights reduced to a vacuum.

Weight $MgCl_2$ .	Weight $AgCl$ .	Atomic weight $Mg$ .
1.33550	4.01952	24.368
1.51601	4.56369	24.350
1.32413	3.98528	24.369
1.40664	4.23297	24.386
1.25487	3.77670	24.373
		Mean, 24.369

The remaining series of experiments are of the usual volumetric character.

#### SECOND SERIES.

Weight $MgCl_2$ .	Weight $Ag$ .	Atomic weight $Mg$ .
2.78284	6.30284	24.395
2.29360	5.19560	24.379
2.36579	5.35989	24.366
		Mean, 24.380

<sup>1</sup> *Ztschr. anorg. Chem.*, 13, 81.

To this series the authors attach less importance than to the others.

### THIRD SERIES.

Weight $\text{MgCl}_2$ .	Weight Ag.	Atomic weight Mg.
1.99276	4.51554	24.349
1.78870	4.05256	24.363
2.12832	4.82174	24.368
2.51483	5.69714	24.372
2.40672	5.45294	24.369
1.95005	4.41747	24.377
		<hr/>
		Mean, 24.365

### FOURTH SERIES.

Weight $\text{MgCl}_2$ .	Weight Ag.	Atomic weight Mg.
2.03402	4.60855	24.360
1.91048	4.32841	24.364
2.09932	4.75635	24.362
1.82041	4.12447	24.362
1.92065	4.35151	24.363
1.11172	2.51876	24.363
		<hr/>
		Mean, 24.362

These values are computed with  $\text{O} = 16$ .

When  $\text{O} = 15.88$ ,  $\text{Mg} = 24.179$ . The last series outweighs all the others.

*Cadmium*.—Hardin's determinations of the atomic weight of cadmium resemble those which he made upon silver. First, the chloride, in solution with potassium cyanide, was electrolyzed in a platinum dish. The weights in this and the other series are all reduced to a vacuum. Computations made with  $\text{Cl} = 35.45$ , and  $\text{O} = 16$ . Data as follows :

Weight $\text{CdCl}_2$ .	Weight Cd.	Atomic weight Cd.
0.43140	0.26422	112.054
0.49165	0.30112	112.052
0.71752	0.43942	112.028
0.72188	0.44208	112.021
0.77264	0.47319	112.036
0.81224	0.49742	112.023
0.90022	0.55135	112.041
1.02072	0.62505	112.002
1.26322	0.77365	112.041
1.52344	0.93315	112.078
		<hr/>
		Mean, 112.038

Secondly, the bromide was treated in the same way. The data were reduced with  $\text{Br} = 79.95$ .

Weight $\text{CdBr}_2$ .	Weight Br.	Atomic weight Cd.
0.57745	0.23790	112.031
0.76412	0.31484	112.052
0.91835	0.37842	112.067
1.01460	0.41808	112.068
1.15074	0.47414	112.053
1.24751	0.51392	112.019
1.25951	0.51905	112.087
1.51805	0.62556	112.076
1.63543	0.67378	112.034
2.15342	0.88722	112.041

Mean, 112.053

In a third series of experiments cadmium was thrown down simultaneously with silver in the same electric current. Weights and results as follows, with  $\text{Ag} = 107.92$ .

Weight Ag.	Weight Cd.	Atomic weight Cd.
0.24335	0.12624	111.928
0.21262	0.11052	111.991
0.24515	0.12720	111.952
0.24331	0.12616	111.916
0.42520	0.22058	111.971

Mean, 111.952

Mean of all the twenty-five experiments,  $\text{Cd} = 112.027$ .

*Mercury.*—Atomic weight also determined electrolytically by Hardin, in the same paper with his work upon silver and cadmium. With the oxide he obtained unsatisfactory results; but with the chloride, bromide, and cyanide he did better. With the chloride, when  $\text{Cl} = 35.45$ , his data, with vacuum weights, are as follows:

Weight $\text{HgCl}_2$ .	Weight Hg.	Atomic weight Hg.
0.45932	0.33912	200.030
0.54735	0.40415	200.099
0.56002	0.41348	200.053
0.63586	0.46941	199.947
0.64365	0.47521	200.026
0.73281	0.54101	199.988
0.86467	0.63840	200.038
1.06776	0.78825	199.946
1.07945	0.79685	199.912
1.51402	1.11780	200.028

Mean, 200.006

With the bromide, when  $\text{Br} = 79.95$ , Hardin found these weights and values :

Weight $\text{HBr}_2$ .	Weight $\text{H}_2$ .	Atomic weight $\text{H}_2$ .
0.70002	0.38892	199.898
0.56430	0.31350	199.876
0.57142	0.31750	199.938
0.77285	0.42932	199.832
0.80930	0.44955	199.814
0.85342	0.47416	199.911
1.11076	0.61708	199.869
1.17270	0.65145	199.840
1.26186	0.70107	199.899
1.40142	0.77870	199.952

Mean, 199.883

With the cyanide, when  $\text{C} = 12.01$  and  $\text{N} = 14.04$ , Hardin found

Weight $\text{HgC}_2\text{N}_2$ .	Weight $\text{Hg}$ .	Atomic weight $\text{Hg}$ .
0.55776	0.44252	200.063
0.63290	0.50215	200.092
0.70652	0.56053	200.038
0.80241	0.63663	200.075
0.65706	0.52130	200.057
0.81678	0.64805	200.103
1.07628	0.85392	200.077
1.22615	0.97282	200.071
1.66225	1.31880	200.057
2.11170	1.67541	200.077

Mean, 200.071

Finally, Hardin made use of Faraday's law, throwing down mercury and silver simultaneously in the same electric current. The equivalent weights are as follows, reduced with  $\text{Ag} = 107.92$ .

Weight $\text{Hg}$	Weight $\text{Ag}$ .	Atomic weight $\text{Ag}$ .
0.06126	0.06610	200.036
0.06190	0.06680	200.007
0.07814	0.08432	200.021
0.10361	0.11181	200.011
0.15201	0.16402	200.061
0.26806	0.28940	199.924
0.82808	0.89388	199.929

Mean, 199.996

The general mean of all four series is

$$\text{Hg} = 199.989.$$

*Tellurium*.—In all determinations hitherto made of the atomic weight of tellurium, the material has been derived from metallic tellurides. Chikashige<sup>1</sup> now gives a series of experiments upon tellurium obtained from Japanese native sulphur, using Brauner's method. The tetrabromide was titrated with solutions of silver, and the following data were obtained. Computations were made upon the basis of  $O = 16$ .

Weight $TeBr_4$ .	Weight Ag.	Atomic weight Te.
4.1812	4.0348	127.57
4.3059	4.1547	127.61
4.5929	4.4314	127.58
		<hr/>
		Mean, 127.587

*Tungsten*.—Schneider<sup>2</sup> objects to the determinations published by Pennington and Smith, regarding them as too high. He attributes their highness to the fact that very small quantities of material were handled, and thinks that there may have been mechanical losses of small particles during the long heating of the substance weighed. He now gives new determinations of his own, with tungstic oxide carefully freed from molybdenum, and made partly by reduction of the oxide, partly by oxidation of the metal. Results as follows, with the percentage of tungsten in tungsten trioxide stated in a third column :

				W in $WO_3$ . Per cent.
2.0728	gram	$WO_3$	gave 1.6450 W	79.323
4.0853	"	"	" 3.2400 "	79.309
6.1547	"	"	" 4.8811 "	79.307
1.5253	"	W	" 1.9232 $WO_3$	79.311
3.1938	"	"	" 4.0273 "	79.304
3.7468	"	"	" 5.9848 "	79.314
				<hr/>
				Mean, 79.311

Hence, with  $O = 16$ ,  $W = 184.007$ .

On the other hand, Shinn,<sup>3</sup> working in Smith's laboratory, obtains some data corroborative of Pennington and Smith. In this series tungsten was oxidized to tungsten trioxide. Results as follows, computed with  $O = 16$ .

<sup>1</sup> *J. Chem. Soc.*, 69, 881.

<sup>2</sup> *J. prakt. Chem.* [2], 53, 288.

<sup>3</sup> Doctoral thesis, University of Pennsylvania, 1896.

						Atomic weight.
0.22297 gram W gave 0.28090 gram WO <sub>3</sub>						184.720
0.17200	"	"	"	0.21664	"	184.964
0.10989	"	"	"	0.13844	"	184.753
0.10005	"	"	"	0.12598	"	185.206
						<hr/>
						Mean, 184.910

The cause of the difference between the values found and those of Schneider is yet to be made out.

My own "Recalculation of the Atomic Weights," a new edition of the work published originally in 1882, is now complete and in the printer's hands. It will probably be published early in 1897, and the following table of values represents the results obtained by combining all the best data :

	H = 1.	O = 16.
Aluminum.....	26.91	27.11
Antimony .....	119.52	120.43
Argon .....	?	?
Arsenic ....	74.44	75.01
Barium.....	136.39	137.43
Bismuth.....	206.54	208.11
Boron .....	10.86	10.95
Bromine.....	79.34	79.95
Cadmium.....	111.10	111.95
Calcium .....	39.76	40.07
Carbon .....	11.92	12.01
Cerium .....	139.10	140.20
Cesium .....	131.89	132.89
Chlorine.....	35.18	35.45
Chromium.....	51.74	52.14
Cobalt.....	58.49	58.93
Columbium.....	93.02	93.73
Copper .....	63.12	63.60
Erbium.....	165.06	166.32
Fluorine.....	18.91	19.06
Gadolinium .....	155.57	156.76
Gallium.....	69.38	69.91
Germanium .....	71.93	72.48
Glucinum .....	9.01	9.08
Gold .....	195.74	197.23
Helium.....	?	?
Hydrogen .....	1.000	1.008
Indium.....	112.99	113.85
Iodine.....	125.89	126.85
Iridium .....	191.66	193.12
Iron.....	55.60	56.02



	H = 1.	O = 16.
Lanthanum.....	137.59	138.64
Lead .....	205.36	206.92
Lithium .....	6.97	7.03
Magnesium.....	24.10	24.28
Manganese .....	54.57	54.99
Mercury.....	198.49	200.00
Molybdenum .....	95.26	95.99
Neodymium .....	139.70	140.80
Nickel.....	58.24	58.69
Nitrogen .....	13.93	14.04
Osmium .....	189.55	190.99
Oxygen.....	15.88	16.00
Palladium .....	105.56	106.36
Phosphorus.....	30.79	31.02
Platinum ....	193.41	194.89
Potassium .....	38.82	39.11
Praseodymium .....	142.50	143.60
Rhodium .....	102.23	103.01
Rubidium .....	84.78	85.43
Ruthenium.....	100.91	101.68
Samarium .....	149.13	150.26
Scandium .....	43.78	44.12
Selenium.....	78.42	79.02
Silicon .....	28.18	28.40
Silver .....	107.11	107.92
Sodium.....	22.88	23.05
Strontium .....	86.95	87.61
Sulphur .....	31.83	32.07
Tantalum.....	181.45	182.84
Tellurium .....	126.52	127.49
Terbium.....	158.80	160.00
Thallium .....	202.61	204.15
Thorium.....	230.87	232.63
Thulium.....	169.40	170.70
Tin.....	118.15	119.05
Titanium .....	47.79	48.15
Tungsten .....	183.43	184.83
Uranium.....	237.77	239.59
Vanadium.....	50.99	51.38
Ytterbium .....	171.88	173.19
Yttrium .....	88.35	89.02
Zinc .....	64.91	65.41
Zirconium.....	89.72	90.40

## ON THE DETERMINATION OF SILICA IN BLAST-FURNACE SLAG.

BY G. H. MEYER.

Received March 13, 1897.

**T**HAT silica is not rendered completely insoluble by one evaporation to dryness with hydrochloric acid, has long been recognized. Several evaporations, even, may not dehydrate traces of silicic acid. Moreover, unless the temperature of drying be carefully regulated, some of the silica may recombine with the bases present and either form highly insoluble silicates, or else go into solution on subsequent treatment with hydrochloric acid. Boiling, concentrated sulphuric acid, on the other hand, is a very efficient agent for the dehydration of silicic acid, Drown's much-used method for silicon in pig iron making use of the fact.

It is the purpose of this article to show that the method of dehydration of silicic acid by sulphuric acid forms a most accurate method for the determination of silica in blast-furnace slags. This arises not only from the fact of the positive and quick production of insoluble silica ; but, what is probably more important, from the very complete decomposition of certain constituents of many slags, and the production of a purer silica than can be otherwise obtained.

Those constituents of slags which have most contributed to inaccuracy in the determination of silica, are spinel (magnesium aluminate)<sup>1</sup> and certain complex titanium compounds. On examples of such slags, accurate determinations of silica could not be made either by direct solution in hydrochloric acid or by solution in hydrochloric acid after fusion with sodium carbonate ; yet the silica was readily determined by application of the simple process described below.

Pure spinel is thoroughly decomposed by fusion, at a high temperature, with a large excess of sodium carbonate. But spinel, when associated with slag, is only decomposed thus with great difficulty.<sup>2</sup> A slag containing as much as five per cent. of spinel residue by ordinary methods, is nevertheless easily decomposed by boiling concentrated sulphuric acid. Considera-

<sup>1</sup> Shimer: This Journal, 16, 501.

<sup>2</sup> Frank Firmstone: Trans. A. I. M. E., 24, 498 et seq., 892 et seq. (The residues there obtained were separated after fusion with sodium carbonate.)

ble experience with a slag, prone to spinel formation, has never shown, even under most favorable conditions for spinel formation, more than this amount in the suddenly cooled slag.

When pure spinel is treated with boiling concentrated sulphuric acid, it "sets" to a hard mass; the surface of the mass being changed to sulphates of magnesium and aluminum, that, being insoluble in the concentrated acid, prevent further decomposition of the spinel. Upon treatment with water these sulphates dissolve. The operation being repeated, more spinel is decomposed; and so on until complete decomposition results.

When the spinel is associated with slag, however, it is decomposed by one treatment with sulphuric acid, probably because of each small particle of spinel in the finely ground slag being separated from the others. Thus, a very difficultly decomposable slag was found to contain about three and one-half per cent. of spinel; but upon determining silica by the method to be given, the silica was found to be almost pure, and the impurities contained no magnesia.

It might be thought that to treat the impure silica from such slags with hydrofluoric acid and weigh the residues would suffice to accurately estimate the silica. This would be the case were it not for the fact that these spinel residues usually contain other compounds. When these compounds contain, as they usually do, some bodies that are changed to new bodies by treatment with hydrofluoric and sulphuric acids, accurate results can only be obtained when the subsequent ignition causes a reversion to the former conditions.

Thus, suppose an impure silica obtained in the course of analysis and containing, among other impurities, an insoluble compound of titanium, aluminum, magnesium, iron, and potash or soda. This impure silica being treated with hydrofluoric and sulphuric acids, the silica would evaporate as silicon tetrafluoride and the bases change to sulphates. Upon igniting strongly, the aluminum, magnesium, and iron would again revert to the original conditions as oxides; but not so with the alkalies. They would either volatilize at a white heat or else remain and retain most of their sulphur trioxide. It is obvious that, under such circumstances, erroneous results for silica would necessarily occur. Below is given a case from actual experience.

Slag No. 1944 was found to give by ordinary methods of analysis, as follows :

	Per cent.
Silica and impurities .....	35.42
Impurities determined by treatment with hydrofluoric and sulphuric acids .....	5.88
Silica .....	29.54

This slag was very exceptional, for although as much as one per cent. of the slag had often been found in the impure silica, never before so much as 5.88 per cent. For the present 29.54 per cent. was considered to be the true proportion of silica in the slag. But in some investigations on spinel, it was noticed that the spinel residues were notably soluble in hot concentrated sulphuric acid. Taking advantage of this fact, the silica was redetermined in this slag, using the new method, with the following result :

	Per cent.
Silica and impurities .....	31.20
Impurities determined by treatment with hydrofluoric and sulphuric acids .....	0.20
Silica .....	31.00

In other words, the former result had been about one and one-half per cent. too low—a very large variation from the truth. A special investigation on this slag showed that after treatment with boiling hydrochloric and hydrofluoric acids there still remained a residue amounting to 3.81 per cent. of the slag. This residue was not entirely decomposed by sulphuric acid (owing probably to changes produced by igniting to burn off filters) ; but, as the above analysis shows, it was readily decomposed by sulphuric acid as it existed in the slag.

The method is as follows: One-half gram of finely ground slag is placed in a four-inch casserole. Cover with cold water (about three cc.) and stir to break up lumps. Then pour into the casserole ten cc. concentrated hydrochloric acid, stirring vigorously to prevent sticking to the bottom.

As soon as the slag seems dissolved as much as it will, and before it has set to a jelly, pour in forty cc. sulphuric acid (one volume concentrated acid to one volume water), stir well, wash off stirring rod, and then cover solution with a funnel.

The funnel should have fused edges and be of such size as to rest upon the sloping inside of the casserole and set down above to the solution.

Place the casserole on a wire gauze and boil rapidly until fumes of sulphur trioxide begin to come from under the edges of the funnel. Cool, dilute somewhat, and clean off the funnel. Add about ten cc. hydrochloric acid and dilute until the casserole is as full as it can be conveniently. Cover with watch-glass and boil gently one minute. Filter on pump. Wash five times with hot hydrochloric acid (sp. gr. 1.10) and five times with hot water. Burn and weigh. The silica is remarkably pure. On "chilled" slags the impurities are from 0.05 to 0.20 per cent.

This method has been carefully compared with a method consisting of two evaporations to dryness with hydrochloric acid, regulating the heat so as not to exceed 120° C., and finally purifying the silica with hydrofluoric acid. The results are generally quite close (the only exceptions being such cases as cited above, where only the sulphuric acid method could give accurate results), the sulphuric acid method giving results somewhat higher, due to the more complete dehydration of silicic acid.

In no case has there been found any evidence of calcium sulphate in the silica when the method is carried out as directed.

TABLE OF RESULTS.

Hydrochloric acid evaporation.	Sulphuric acid evaporation.
36.00	36.06
35.52	35.62
34.24	34.74
35.76	35.96

The time necessary is about one and one-half hours, and there is very little attention required. "Chilled" slag is best suited, but the method will be found successful on many slowly cooled slags that are very insoluble in hydrochloric acid. Unfortunately, the method is only useful for the determination of silica. Attempts to determine readily alumina and lime in the filtrate from the silica have all failed. Results are much too low.

It is worthy of note that the silica obtained is very dense and hard. This is an advantage, in that there is little danger of loss of the silica, due to its being thrown out of the crucible by the gases escaping while the filter is charring. With the silica

ordinarily obtained, this mechanical loss is very apt to occur. The silica obtained by this method is, however, more difficult to decompose by treatment with hydrofluoric acid. It is much less hygroscopic and weighings are thus more accurately made.

For as many slags as have been investigated there is claimed for the above method (1) greater accuracy due to more complete dehydration of silicic acid, and thorough decomposition of certain slag constituents, and (2) greater rapidity and ease of execution than for other methods of about equal accuracy.

LABORATORY OF ANDOVER IRON CO.,  
March 13, 1897.

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## THE DETERMINATION OF LEAD IN LEAD ORES.<sup>1</sup>

BY RICHARD K. MEADE.

Received March 8, 1897.

**I**N the wet assay of lead ores, the general mode of procedure seems to be to precipitate the lead as a sulphate by dissolving the ore in a mixture of sulphuric and nitric acids and evaporating until the solution is free from the latter acid. The residue, consisting of the precipitated lead sulphate and gangue, is collected upon a filter paper and, after washing, is dissolved in either ammonium tartrate or acetate or in sodium thiosulphate; then precipitated as an oxalate or chromate and determined volumetrically, or precipitated as a sulphide and estimated gravimetrically. Another way is to ignite the residue of lead sulphate and gangue and weigh. Then treat with ammonium tartrate or acetate, and collecting whatever residue remains, ignite and weigh. The difference between these two weights is taken as lead sulphate.

Of these methods the first is rather inaccurate.<sup>2</sup> The third is rather slow, and both are inapplicable when calcium, barium, and strontium are present. The second is the most accurate of the three outlined above, but is also the slowest.

While recently working upon some specimens of galena, the writer thought of a simple method for determining the amount of lead in this mineral, and in lead ores in general. Like two of the above methods, it fails in accuracy when barium, strontium, and small amounts of calcium are present, since these

<sup>1</sup> Read at the meeting of the New York Section, March 5, 1897.

<sup>2</sup> See Sutton: "Systematic Handbook of Volumetric Analysis," Sec. 66, 1 and 2.

metals are precipitated by sulphuric acid, and would be weighed along with and calculated as lead, causing too high results. In detail the method is as follows :

*Method.*—Weigh one gram of the ore if rich, more if poor, into a platinum dish, cover with a watch-glass and add forty to fifty cc. of a mixture of one part sulphuric acid (1.84 sp. gr.) and three parts nitric acid (1.42 sp. gr.). Heat the covered dish on a hot plate, water-bath, or sand-bath until the action of the acids on the ore has apparently ceased. Then remove the watch-glass and rinse into the dish. Add ten to fifteen cc. hydrofluoric acid to the solution and evaporate until dense white fumes of sulphuric acid begin to come off. It is better to conduct the evaporation under a hood for obvious reasons. Remove the dish from the source of heat and cool. Dilute to about 100 cc. with water, digest until all soluble salts are in solution and filter, washing first with a two per cent. solution of sulphuric acid and then with alcohol. Dry, burn filter paper, and ignite precipitate separately. Weigh as lead sulphate and calculate per cent. of lead present in the ore.

To test the method several lead-bearing minerals were carefully assayed for lead by the method (A) outlined by Fresenius (Quant. Anal., 213), and then by the above method (B), after ascertaining that calcium, barium, and strontium were absent, with the following results :

	Method A. Per cent. lead.	Method B. Per cent. lead.
Galenite.....	77.34	77.46
Pyromorphite .....	75.26	75.35
Cerussite .....	76.46	76.53

To further test the method, and especially to see if any lead was lost by volatilization as a fluoride, a solution of lead nitrate was made. Twenty-five cc. of this solution, on evaporation with sulphuric acid, gave 0.4297 gram of lead sulphate as an average of six determinations.

The same quantity, on evaporation with sulphuric and hydrofluoric acids, gave 0.4280 gram of lead sulphate as an average of six determinations.

Twenty-five cc. of the solution, to which two-tenths gram of silica was added, on evaporation with hydrofluoric and sulphuric

acids, gave 0.4285 gram of lead sulphate as an average of six determinations.

Fearing that the stock solution might be too concentrated and that small errors in delivering exactly the same quantity each time from the pipette might be the cause of discrepancy in the results, a new and more dilute solution was made, and 100 cc. of this used in each experiment. Below are the results expressed in grams of lead sulphate :

	On evaporating with sulphuric acid alone.	On evaporating with silica and sulphuric and hydrofluoric acids.
1 .....	0.4154	0.4131
2 .....	0.4147	0.4136
3 .....	0.4150	0.4142
4 . . . . .	0.4156	0.4136
Average .....	0.4151	0.4136

It will be seen that, in all experiments, the results are higher when sulphuric acid alone was used than when hydrofluoric acid was added. Thinking that there was a loss of lead by volatilization as a fluoride, one gram of pure lead sulphate was heated in a platinum crucible to drive off moisture, etc., and, after cooling, both crucible and contents were weighed. The crucible was then half filled with hydrofluoric acid, a few drops of sulphuric acid added, the whole placed over a lamp and the acid driven off. After being gently ignited and cooled, the crucible and contents were weighed, then ignited and weighed again until the weight was constant. The lead sulphate was found to have suffered no loss by volatilization as a fluoride; for the crucible and contents weighed exactly the same after as before treatment with the acids. This experiment was repeated with identically the same results. We deemed these two experiments sufficient proof that no lead should be lost in this method by volatilization as a fluoride.

The possibility of the stock solution containing silica in solution, along with the lead nitrate, causing the higher results to be found in the left hand column, suggested itself. To ascertain if this was the case, two of the residues from the evaporation with sulphuric acid alone, were brushed into a beaker and treated with ammonium tartrate. They dissolved completely, the residue only weighing 0.0003 gram after the weight of the



filter ash had been subtracted. This experiment was also repeated with similar results, proving the purity from silica of the lead sulphate precipitate.

We believe the foregoing experiments test the method fairly and rigidly, and that chemists will be safe in using the above when they know metals precipitated by sulphuric acid as sulphates or oxidized by nitric acid to insoluble compounds are absent.

Barium and strontium are rarely found associated with lead. Calcium, when present in galena as calcite, may be gotten rid of by first treating the ore with hydrochloric acid and filtering. The filtrate will contain the calcium; the residue will hold the lead and may be treated with hydrofluoric, sulphuric, and nitric acids, and the process carried out as above.

When the ore contains calcium, in small quantities only, the latter may be hindered from interfering with accurate results by washing the precipitated lead sulphate four or five times by decantation and then thoroughly upon the filter with a two per cent. solution of sulphuric acid. The calcium sulphate, being slightly soluble in the acid solution, is carried off by the wash water. The writer has found it possible to remove as much as four per cent. of calcium sulphate by this means.

The analysis of a lead ore can be made very nearly as quickly by this method as volumetrically and much more satisfactorily.

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## NOTE ON THE SEPARATION OF SILICIC AND TUNGSTIC ACIDS.

BY JAMES S. DE BENNEVILLE.

Received March 20, 1897.

THE object of the present note is to call attention to an important observation made by Mr. Lawrence Dufty in reference to the determination of silicon in tungsten steel and ferrotungsten. A common method for making such determination is to dissolve the tungstic oxide on the filter by means of hot dilute ammonia and to so obtain the silica at once for determination. Karsten<sup>1</sup> had pointed out the solubility of freshly pre-

<sup>1</sup> *Ann. der Phys. (Pogg.)*, 6, 357, 1826.

precipitated silicic acid in ammonia, and Pribram<sup>1</sup> and later Sonchay<sup>2</sup> had shown that even ignited amorphous silica was perceptibly soluble in this alkaline reagent. Mr. Dufty<sup>3</sup> showed that in dealing with the small quantities of silicon found in ferrotungsten and in tungsten steels this solubility of the silica renders the ammonia method incorrect and misleading. To his results, as given by Professor Arnold, it can be added that the remarks apply equally well to cold ammonia. Solution of ore or alloy, evaporation to dryness, re-solution and filtration of the mixed oxides from the soluble material is conducted in the usual manner. The experimental results given in Tables I and II were obtained with a ferromanganese containing nearly seven per cent. of tungsten. In the figures given, the solubility of the silica is not so great as compared with Mr. Dufty's results. If the residue, dried on the center of the stove, is burnt over the naked flame, this solubility is still further reduced; but in such case the quantity of tungstic oxide insoluble in ammonia is greater than when the residue is simply baked. Also, evaporation with hydrofluoric acid alone does not cause any loss of tungsten; but the addition of a few drops of sulphuric acid apparently insures the complete expulsion of the silica more readily than when hydrofluoric acid is used alone. The advantage, therefore, of weighing the total oxides and volatilizing the silica, as recommended by Professor Arnold, is obvious. In mineral analysis, and particularly in the preparation of pure tungstic oxide, the reaction of silica with ammonia is an important one; for only the crystallized ammonium tungstate is free from silica. A wolframite containing 65.5 per cent. tungsten trioxide, and by the volatilization method 5.61 per cent. silica, gave on dissolving the tungstic oxide from silica by ammonia (1) insoluble silica 3.84 per cent., and soluble silica 1.64 per cent., and (2) insoluble silica 3.22 per cent. and soluble silica 2.20 per cent. The silica belongs mainly to intermixed mica.

<sup>1</sup> *Ztschr. anal. Chem.* (Abstract), 6, 119, 1867.

<sup>2</sup> *Ibid.*, 11, 182, 1872.

<sup>3</sup> Cited by Professor T. O. Arnold: "Steel Works Analysis," pp. 136-138. Whittaker & Co., London, 1895.

## FERROMANGANESE CONTAINING TUNGSTEN.

*I. Residue Baked to Dust Dryness on the Stove.*

Treatment.	HF1.	HF1 + H <sub>2</sub> SO <sub>4</sub> .	HF1 + H <sub>2</sub> SO <sub>4</sub> .	HF1.	HF1 + H <sub>2</sub> SO <sub>4</sub> .	HNO <sub>3</sub> + HCl.
Silica regained by one evaporation.....	0.0040	0.0022	0.0059	0.0038	0.0035	....
Silica regained by two evaporations ....	0.0058	0.0024	0.0057	0.0049	0.0036	....
Silica regained by three evaporations ....	0.0065	0.0022	0.0055	0.0051	0.0036	....
Silica regained by four evaporations ....	0.0062	....	....	0.0055	....	....
Total silicon regained	0.0030	0.0010	0.0026	0.0026	0.0017	....
Per cent. total silicon	21.7	7.0	19.0	18.2	12.8	....
Total silicon in the alloy.....	0.0139	0.0141	0.0137	0.0143	0.0133	0.0141

*II. Residue Burnt over the Flame.*

Treatment.	HF1.	HF1 + H <sub>2</sub> SO <sub>4</sub> .	HF1.	HF1.	HF1 + H <sub>2</sub> SO <sub>4</sub> .	HF1.
Silica regained by one evaporation.....	0.0008	0.0016	0.0014	0.0006	0.0022	0.0037
Silica regained by two evaporations ....	0.0010	0.0016	0.0020	0.0004	0.0024	0.0037
Silica reg'n'd by three evaporations ....	0.0010	....	0.0020	....	0.0024	....
Silica regained by four evaporations ....	0.0009	....	0.0022	....	....	....
Total silicon regained	0.0005	0.0007	0.0010	0.0003	0.0011	0.0017
Per cent. total silicon	3.62	5.11	6.86	2.11	8.09	....
Total silicon in the alloy .....	0.0138	0.0137	0.0145	0.0142	0.0136	....

In both tables the figures refer to the silica recovered from the ignited tungstic oxide which has been "separated" by digestion with cold ammonia solution.

THE ELECTROLYTIC DETERMINATION OF CADMIUM.<sup>1</sup>

BY S. AVERY AND BENTON DALES.

Received March 23, 1897.

THE work here presented grew out of an effort to find a practical method for determining this metal. The usual methods often fail to give satisfactory results, and, while we have not succeeded in finding an ideal method, we hope that the experiments here given will be of interest.

<sup>1</sup> Read at the meeting of the Nebraska Section, March 19, 1897.

The double oxalate method presents the following difficulties: It is not always easy to get and keep a clear solution. The plate is apt to oxidize if not very carefully treated, and the last traces of cadmium are hard to eliminate from the solution. Several determinations were made by this method. In each one a solution containing 0.0641 gram of cadmium was taken. A small storage battery of four volts furnished the current, which varied from two-tenths to one-half ampère. The time of each was from fourteen to eighteen hours.

	Cadmium found. Gram.
No. 1.....	0.0615
No. 2.....	0.0658
No. 3.....	0.0613

We then tried the precipitation in acetic acid solution in the hope of finding a more serviceable method. The result was in complete harmony with the experiments of Heidenreich. He says,<sup>1</sup> "The separation of cadmium from acetic acid solutions did not give satisfactory results. By adding ten cc. of fifty per cent. acetic acid to 120 cc. of the solution, and using a current of four-tenths ampère at a tension of seven and a half volts, the cadmium separated out in the form of leaf-like crystals. Experiments conducted with less acetic acid and with less current at a lower tension (two to ten cc. acetic acid, one-tenth to four-tenths ampère, four to seven and a half volts) at various temperatures, also gave no serviceable results."

Solutions which contained either phosphoric acid or sulphuric acid were also found to be unsatisfactory.

The cyanide solution seems to us best adapted to the determination of cadmium where more than one-tenth gram of the metal is present (solution 150–200 cc. and area of electrode for plating 100–150 sq. cm.) The usual objections to a cyanide solution may be mentioned. The solution offers an enormous resistance, hence a strong current is necessary. The last traces of the metal are hard to precipitate, and finally these solutions are exceedingly unpleasant to manipulate. A solution containing 0.0452 gram of cadmium as the double potassium cyanide was placed in a current from a thermopile for twenty-four hours. The thermopile has a tension of four volts and shows

<sup>1</sup> *Ber. d. chem. Ges.*, 29, 1587.

an ampèrage of two when no resistance other than the ampèremeter is inserted. 0.0446 gram of cadmium was precipitated.

#### DETERMINATION OF CADMIUM IN FORMATE SOLUTION.

The excellent results that zinc gives when determined in a formate solution<sup>1</sup> suggested to us that cadmium might be satisfactorily determined in a similar manner. The results are perfectly satisfactory provided certain conditions are rigidly maintained. There should be not more than one-tenth gram of metal in 150 cc. of solution. This amount of metal should be deposited on a surface of not less than 100 sq. cm. The voltage should not exceed three and four-tenths, and the ampèrage 0.15-0.20.

The solution of cadmium was made as follows: Chemically pure cadmium nitrate was converted into the oxide, which, in turn, was reduced, in a current of hydrogen, to the metal. The latter was then placed in a hard glass tube bent into the shape of W. The metal was placed in the first bend and distilled into the second in a current of hydrogen. The distillate thus obtained showed no trace of silica or other impurities. A weighed quantity of this distilled cadmium was dissolved in dilute sulphuric acid, placed in a measuring flask, and diluted to the mark. Portions of this solution were measured out from a burette. The weights, measuring flask, and burette used were carefully calibrated.

The source of the current was the thermopile. The precipitation was made with platinum dishes or cones in the usual manner. The average time was twenty-four hours.

The following is given as a representative determination. To a solution of cadmium sulphate six cc. of formic acid, sp. gr. 1.20, was added. Potassium carbonate was then added until a slight permanent precipitate formed. This precipitate was just dissolved in formic acid, then one cc. excess of the latter added. Next the solution was diluted to 150 cc. The solution was then put in a weighed platinum dish and placed in the current generated by the thermopile. The meters in the first determination read as follows:

Time.	Ampère.	Volts.
5 P.M. ....	0.1	2.6
10 P.M. ....	0.1	2.6

<sup>1</sup> This Journal, 18, 654.

The next morning the resistance of the rheostat was diminished from time to time.

Time.	Ampère.	Volts.
9 A.M. ....	0.125	3.0
12 M. ....	0.105	3.1
5 P.M. ....	0.195	3.3

Determination.	Weight of cadmium taken. Gram.	Weight of cadmium found. Gram.
1	0.0454	0.0452
2	0.0454	0.0454
3	0.0642	0.0642
4	0.0642	0.0642
5	0.0642	0.0641

A large number of determinations were made in more concentrated solutions, also with stronger currents, but these often failed to give a good adherent plate of the metal. The plates formed in the determinations given showed no tendency to oxidize and they could be kept for several days in the desiccator without change of weight.

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## THE NORMAL URINE.

BY CHARLES PLATT.

Received March 12, 1897.

THE various compilations current as "Text-books of Urine Analysis," differ materially in their statements as to the average composition of a normal urine. In many cases, indeed, the authors have not even attempted to reconcile their "totals" with the figures given for individual constituents, but aside from this, which is, of course, the result of carelessness on the part of the compiler, we find great variations in the original figures, due not so much to errors of determination as to failure to secure representative samples for analysis. Normals determined for one nationality, or for one class of one nationality, are commonly applied indiscriminately to all without regard to fundamental conditions. For instance, the average American's is not that of the German student, and yet it is a majority of figures given in our text-books have the observations of German professors, working with their student assistants.

In view of this laxity in text-book statement, the writer has for several years made careful records of all urine analyses with due attention to the age, sex, and health of the individuals supplying the samples, and these figures (in all cases compared with and in some cases averaged with those of foreign observers) are now given in the following table: <sup>1</sup>

## THE NORMAL URINE.

Color.....	Pale-amber, straw-yellow.
Appearance.....	Clear or with faint cloud of mucus.
Odor .....	"Aromatic."
Reaction .....	Acid. Acidity in 24 hours equivalent to 2-4 grams oxalic acid.
Specific gravity at 15° C..	Range for adults, 1.015-1.025. Averages: Man, 1.020; Woman, 1.018.
Quantity .....	1100-1600 cc. in 24 hours. Averages: Man, 1450 cc. (22 cc. per kilo of body-weight); woman, 1250 cc.

	Normal urine. Grams.	Averages for adults.		
		Man.		Woman.
		Grams urine in 24 hrs.	Grams per kilogram of body- weight.	Grams urine in 24 hrs.
Total solids.....	45.0 -65.0	60.0	0.91	51.0
Urea.....	20.0 -50.0	34.0	0.51	30.0
Uric acid .....	0.3 -0.8	0.6	0.009	0.5
Creatinin .....	0.4 -1.3	0.9	0.014	0.8
Hippuric acid .....	0.4 -1.0	0.7	0.010	0.6
Xanthine, sarcine, etc .....	0.001-0.010	0.005	....	..
Oxalic acid.....	0.020-0.030	0.025	....	..
Glycero-phosphoric acid.....	0.010-0.020	0.015	....	..
Propionic, valeric, caproic, and butyric acids.....	0.008-0.080	0.040	....	..
Phenol, cresol, etc.. ..	0.005-0.020	0.010	....	..
Sulphur dioxide in ethereal sulphates.....	0.090-0.500	0.250	....	..
Indoxyl sulphuric acid (calculated as indigo).....	0.005-0.019	0.008	....	..
Thiocyanic acid.....	0.001-0.008	0.004	....	..

<sup>1</sup> Authors consulted: J. Vogel, Loebisch, Kerner, Daiber, Hammarsten, Neubauer, Pfäfer, Voit, Salkowski, Liebermann, Brieger, Hoffmann, Dragendorff, Munk, Hoppe-Seyler, Yvon and Berlios, Lehmann, Uhle, Ranke, Furbringer, Geschleiden, Moritz, von Jacksch, Planer and Morin, Magnier, Robuteau, Gautier, Becquerel, Méhu, Halliburton, Charles, Parkes, Black, Bence-Jones, Tidy and Woodman, Beale, Parrot, Breed, Oliver, Thudichum, Weidner, Purdy, Tyson, Grüner, Jaffé, Rankin, von Franque, Oppenheim and Meyer.

	Normal urine. Grams.	Averages for adults.		
		Man.	Woman.	
		Grams urine in 24 hrs.	Grams per kilogram of body- weight.	Grams urine in 24 hrs.
Paraoxyphenylacetic, paraoxyphenylpropionic, dioxyphenylacetic, and paraoxyphenylglycollic acids	0.010-0.030	0.020	....	..
Bile salts.....	0.0 -0.010	0.008	....	..
Urobilin, urochrome, etc.....	0.080-0.140	0.125	....	..
Carbohydrates.....	0.014-0.075	0.044	....	..
(Reducing power of normal urine equivalent to an average of three-tenths of one per cent. glucose).				
Sarco-lactic, succinic, glycuronic, and oxaluric acids, acetone, inosite, cystin, taurin, uro-rubinogen, uro-rubin, pigment of Giacomini, scatoxylsulphuric acid (often in considerable amount), scatoxylglycuronic acid; nephrozymase, pepsin, and other ferments; pseudoxanthine, paraxanthine, heteroxanthine, guanine, adenine, etc.; pyrocatechin, hydroquinone, protocatechuic acid, etc.....	traces	....	....	..
Chlorine.....	5.0 -10.0	7.3	0.110	6.0
Phosphorus pentoxide .....	2.0 - 3.5	3.0	0.045	2.5
Sulphur trioxide.....	1.5 - 3.0	2.2	0.033	1.9
Potassium oxide.....	2.5 - 3.5	3.0	0.045	2.8
Sodium oxide.....	4.0 - 6.0	4.5	0.068	4.0
Ammonia.....	0.5 - 0.8	0.72	0.010	0.6
Calcium oxide.....	0.2 - 0.4	0.30	0.0045	0.28
Magnesium oxide.....	0.3 - 0.5	0.40	0.0066	0.35
Iron.....	0.001-0.010	0.007	....	..
Silicic acid, carbonic acid, hydrogen peroxide, nitrates, nitrites, and metals; <i>e. g.</i> , manganese and copper.....	traces	....	....	..

GASES<sup>1</sup> IN NORMAL URINE.

	In 100 volumes of gas. cc.	In one liter of urine. cc.
Carbon dioxide .....	65.40	15.957
Oxygen.....	2.74	0.658
Nitrogen.....	31.86	7.775
	<hr/> 100.00	<hr/> 24.390

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<sup>1</sup> Morin, after Loebisch.



# **NOTE ON THE VOLATILITY OF BORIC ACID; SEPARATION OF BORIC FROM PHOSPHORIC ACID; ESTIMATION OF BORIC ACID IN FOODS.**

**BY L. DE KONINGH.**

**March 1, 1897.**

**W**HEN titrating boric acid with standard soda, any alkali must be first neutralized by means of a mineral acid and the solution well boiled to expel any carbon dioxide. As it is generally believed that boric acid is volatile and escapes with the aqueous vapors, it was thought worth while to ascertain in how far this is serious enough to interfere with accurate analysis. Some chemists advise boiling under an upright condenser, but the writer doubts whether one gets really rid of the carbon dioxide, which is the great enemy when titrating with phenolphthalein as indicator. In the first set of experiments two grams of commercial boric acid were dissolved up to one liter. One hundred cc. were mixed with fifty cc. pure glycerol, phenolphthalein was added and two-tenths normal soda was run in until a permanent red coloration was obtained, which took place after adding 16.3 cc. One hundred cc. were now boiled for five minutes, and after cooling, made up again to 100 cc., sixteen cc. having evaporated. This time 16.1 cc. of the soda were required. One hundred cc. were again boiled, this time for ten minutes, the loss being fifty cc.; 16.0 cc. of soda were required. In a third experiment the boiling lasted fifteen minutes, the loss amounting to sixty cc.; sixteen cc. of soda were consumed. These three experiments were conducted in a narrow-necked conical flask; the fourth experiment was therefore conducted in a large beaker, boiling for fifteen minutes, the loss now amounting to eighty cc.; sixteen cc. of soda were required.

In the second set of experiments two grams of boric acid were dissolved with the aid of fifty grams of dry sodium carbonate and the solution made up to one liter. One hundred cc. were colored with methyl orange and slightly acidified with hydrochloric acid. After boiling for three minutes the loss amounted to three cc. After cooling the liquid was carefully neutralized and then mixed with fifty cc. of glycerol. After adding phenolphthalein 16.6 cc. of approximately two-tenths normal soda were required. Another 100 cc. were treated in the same way, the boiling last-

ing ten minutes, and the loss amounting to thirty-seven cc., when 16.6 cc. of soda were required. In a third experiment the boiling was continued for fifteen minutes, the loss amounting to sixty cc. ; again 16.6 cc. of soda were required. From these experiments, it may be safely concluded that dilute solutions of boric acid may be boiled down to a small bulk without any loss of the acid.

To see what the loss would amount to if actually evaporated to dryness, two portions of 100 cc. each, one with addition of some sodium silicate, were mixed with a large excess of hydrochloric acid and the mixture treated as in a silicate analysis. After dissolving in about 100 cc. of water and removing the trace of free acidity, the one with the silica added took 14.8 and the other 13.6 cc. of soda. It is, therefore, plain that when nearly dry a considerable loss takes place by volatilization, but it is much less than some authors would have us believe.

#### SEPARATION OF BORIC FROM PHOSPHORIC ACID.

It has been pointed out in a previous communication<sup>1</sup> that the great, if not the only, drawback of using the titration process for estimating the boric acid in foods, is the invariable presence of phosphoric acid in the ash of the same. It may, therefore, be argued that once given a good process for removing phosphoric acid, the estimation of boric acid in foods may be considered as completely solved for the present. Thomson,<sup>2</sup> the inventor of the titration process, has proposed using barium chloride, but has to my knowledge never finished his researches in that direction. Another writer has proposed using calcium chloride, and this may be used with some success as follows: The solution must contain a slight excess of sodium carbonate. On cautiously adding calcium chloride, any phosphate, and also the excess of carbonate, is precipitated, while the borate in very dilute solution is not precipitated at all. On now adding solution of ammonium carbonate containing excess of ammonia, the excess of lime is precipitated and the filtrate contains boric acid with free ammonia and ammonium chloride. By boiling with due excess of sodium carbonate the ammonia compounds are soon expelled, as the liquid contains an alkaline borate which is then titrated as directed.

<sup>1</sup> This Journal, 19, 55.

<sup>2</sup> *J. Soc. Chem. Ind.*, 12, 432.

One hundred cc. of the solution mentioned in the first set of experiments were mixed with ten drops of saturated solution of sodium phosphate. It finally took 16.3 cc. of soda solution, showing the method to be accurate. The separation by means of magnesia mixture was also tried. Another 100 cc. of the solution were acidified with hydrochloric acid and then mixed, as usual, with slight excess of magnesia mixture, ten drops of sodium phosphate solution having been previously added. After some hours the liquid was filtered and then mixed with about five grams of sodium carbonate. On warming, the bulk of the magnesia was at once precipitated and filtered off to prevent bumping. The liquid was now rapidly boiled down to expel ammonium compounds, and finally evaporated to dryness to render the magnesia insoluble. After taking up with a little water and filtering, the result finally was 16.2 cc. of soda solution.

#### ACTION OF AMMONIACAL SOLUTION OF ZINC OXIDE ON BORIC ACID.

If boric acid is mixed with large excess of zinc oxide dissolved in ammonia, and then evaporated until no more ammonia is given off, the separated matter seems to be pure zinc oxide; at all events when dissolved in sulphuric acid and mixed with alcohol the latter does not burn with a green flame; the filtrate also gives no precipitate with ammonium sulphide. Fifty cc. of the first boric acid solution treated with ammoniacal zinc took finally eight cc. of soda. Experiments are being made, but as yet without much success, in rendering this a process for the separation of the phosphoric acid, which as we know forms an insoluble compound with zinc. Now the question arises: Can one, without hesitation, recommend the titration process as fit for the estimation of boric acid in foods? In a few experiments in which one-tenth gram of crystallized boric acid (dissolved in soda-lye) was introduced into 100 grams of oatmeal, 0.095 gram was recovered by the magnesia separation; but the word "food" comprises such a variety of bodies that in some cases unexpected difficulties may turn up. However, the writer intends always using it when opportunity arises, and by adding a known extra weight of the acid to another portion of the substance under examination, hopes before very long to bring forward a

further series of experiments; and in the meanwhile invites others to do the same and to publish their results in this Journal.

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## METHOD OF DRYING SENSITIVE ORGANIC SUBSTANCES.<sup>1</sup>

BY C. C. PARSONS.

Received March 18, 1897.

SOME years ago in preparing formulas for a class of detergent compounds, of which soap was one of the ingredients, it was necessary, in order that the formula should be exact and definite, to ascertain the moisture in a great number of soaps, as commercial soaps differ greatly in this particular.

The usual processes described in analytical works were slow, and, unless very carefully conducted, were liable to cause decomposition of the soap by overheating.

Some previous experiments in dissolving soaps in mineral oils for increasing their viscosity and lubricating quality, suggested using an oil-bath, putting the soap directly into the hot oil, and weighing before and after the hot oil had driven off the moisture. It worked very satisfactorily, and subsequently was used with equally good results for drying wood paper pulp in some investigations in nitrating it for a smokeless powder.

The process has not been used extensively for commercial analysis, but in factory operations it has been used continually for some years, and could possibly be applied to drying many other substances.

In practice the best results have been obtained by using what is commercially called a straight paraffin oil, that is without any mixture of animal or vegetable oils or fats, or mineral substances, perfectly neutral, 0.920 specific gravity (22.5° B.), 435° flash test, 500° fire test, about 550° boiling-point. The object of a high fire test is that the oil will be so freed from volatile matter that none of it will be carried off with the moisture in the substance to be dried.

If many such analyses are required, it is advisable to prepare enough oil for several operations by heating it to about 250° for some time, and then keep it in a closed vessel, as it absorbs moisture from the air when exposed. A suitable amount of the sub-

<sup>1</sup> Read at the Meeting of the New York Section, March 5, 1897.

stance to be dried should be divided into small, thin pieces, then about six times its weight of oil put into an evaporating dish, and placed in a drying closet kept at  $240^{\circ}$ . When the oil has the temperature of the drying room, it should be weighed, and the substance to be dried, weighed and added to it. If very moist, add in successive portions. There will be a slight effervescence at first, and the whole should be kept in the drying closet for a few minutes after the effervescence has ceased.

Ordinarily the whole operation may be completed in twenty minutes. The evaporating dish containing the oil, and the substance, which is now perfectly dry, should be weighed; the loss, of course, is the moisture.

Substances like soaps, portions of which are dissolved in the oil, cannot be recovered, but those like wood pulp, none of the constituents of which are soluble in the oil, can be put in an extractor, and, after the oil is washed out, weighed again if desired.

The advantages of this process are, the quickness with which the operation may be carried out, simplicity of apparatus, ease of manipulation, and the fact that the substance to be dried is perfectly protected from any action of the air, by being immersed in a neutral liquid while heated, so that it will stand a higher temperature, without decomposition, insuring perfect dryness, than would be possible if exposed to the air.

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## THE VOLUMETRIC DETERMINATION OF LEAD.<sup>1</sup>

BY J. H. WAINWRIGHT.

Received March 8, 1897.

HAVING been called upon some time ago to determine the percentage of metallic lead in a large number of samples of "white lead," "litharge," "red lead," etc., in a limited time, it became extremely desirable to find, if possible, some simple and rapid method, whereby twenty or thirty samples could be finished in a day. Extreme accuracy was not particularly necessary, since an error of two to three-tenths per cent. either way would not materially vitiate the results for the purpose for which they were required.

Various volumetric methods were examined, but they all with

<sup>1</sup> Read at the meeting of the New York Section, March 5, 1897.

one exception proved very unsatisfactory and offered no advantages whatever over the conventional gravimetric methods of precipitation and weighing the lead, either in the form of sulphate or as chromate. This one exception is the method described in Crookes' Select Methods, slightly modified, and which consists, according to Crookes, in adding an excess of sodium acetate to a neutral solution of a lead salt (nitrate carefully neutralized with either ammonia or sodium carbonate) and titrating this solution with a standardized solution of potassium bicarbonate, one cc. of which should equal 0.0207 gram metallic lead, the end of the reaction being determined by the production of the characteristic red silver chromate upon adding a drop of the solution to a drop of silver nitrate solution upon a porcelain plate. Following out this method, as described by Crookes, concordant results are difficult to obtain, but by slightly modifying some of its details, it appears to leave nothing to be desired for certain classes of work.

For the determination of metallic lead in litharge, for example, the assay is proceeded with as follows: 1.00 to 1.25 grams is dissolved in ten to fifteen cc. nitric acid (sp. gr. 1.20), the solution is neutralized with ammonia in excess and a considerable excess of acetic acid is added. It is then allowed to boil and the potassium bichromate solution is run in from a burette graduated to one-tenth cc. After the addition of bichromate solution sufficient to precipitate nearly all the lead, the solution should be again boiled until the precipitate of lead chromate, which at first is bright yellow, has become orange colored. The titration is now continued one-half cc. or so at a time, the solution being well stirred after each addition of bichromate until the reaction is almost complete, which can be observed by the sudden clearing up of the solution, the lead chromate settling promptly to the bottom of the beaker. This will, if the solution is hot, usually occur when within about one cc. of the end of the reaction, which should now be completed drop by drop, stirring and allowing to settle after each addition of bichromate and testing by adding a drop or two of the supernatant liquid to a drop of silver nitrate solution on a white porcelain plate or tile until a distinct red color is produced.

The solution of bichromate should be made of such a strength

that one cc. equals not much more nor less than 0.01 gram metallic lead and should be standardized either by means of the pure metal or by means of a pure "white lead" in which the metal has been very accurately determined gravimetrically.

The points to be particularly observed and which appear to be essential to the success of the method are :

*First.*—The solution of the lead salt should be as concentrated as possible before titration and decidedly acid with acetic acid.

*Second.*—It should be free from other metals, especially such as may exist in the lower forms of oxidation ; antimony and tin unless they have been previously thoroughly oxidized by repeated evaporation with fuming nitric acid are particularly to be avoided, since they appear to reduce the bichromate, and the results of the titration will therefore be much too high in terms of lead. Bismuth, which like lead is precipitated as a chromate, should also be avoided.

*Third.*—The titration should be performed in a solution kept at all times as near the boiling-point as possible.

*Fourth.* — The bichromate solution should be neither too strong nor too weak for obvious reasons. As given in Crookes' Select Methods the solution appears to be much too strong since, unless an inconveniently large weight of the sample is taken, the experimental error is too great. On the other hand, it should be strong enough for a drop or two in excess, in a solution of about 100 to 120 cc. to react readily with the silver nitrate. The strength as given above (*i. e.* about 0.01 gram lead per cc.) is approximately correct.

*Fifth.*—The test solution of silver nitrate should be dilute, not over two to three per cent.

The method is particularly adapted to the assay of such substances as white lead, red lead, litharge, pig lead, etc., and for lead ores wherein the lead exists as carbonate, etc. In the case of "red lead," solution should be effected by means of nitric acid (sp. gr. 1.20), boiling, and then adding drop by drop from a pipette, a dilute solution of oxalic acid until the lead oxide formed is completely dissolved. If the "red lead" contains organic matter, as is often the case with some samples of vermilion to which a small amount of a dye has been added, the solution should be filtered before the titration. "White

lead'' may be dissolved directly in dilute acetic acid and the resulting solution titrated without filtration. The method can also be used sometimes to advantage in the case of alloys containing tin and antimony, and with impure lead bullion, but the sample must be thoroughly oxidized and the solution filtered before titration, and in the latter case it is desirable before filtration to precipitate whatever silver there may be present by means of a drop or two of hydrochloric acid or solution of sodium chloride. The small amount of chloride present in the resulting lead solution does not materially interfere with the end-reaction provided, as mentioned by Crookes, the size of the drops of silver nitrate solution spread upon the porcelain plate be somewhat increased.

The following are some of the results obtained by this method:

STANDARDS.		
Lead. Gram.	Potassium carbonate solution. cc.	One cc. = gram lead. Gram.
0.6475	56.3	0.01150
0.6330	54.8	0.01155
0.6234	54.1	0.01152
0.6196	89.1	0.00690
0.6475	94.0	0.00696
0.6706	96.4	0.00706
0.4911	46.1	0.01065
0.5654	53.5	0.01056
0.5800	54.7	0.01060
0.5355	50.6	0.01058
0.4216	39.9	0.01056
0.4673	42.2	0.01057
0.5061	29.0	0.01742
0.5387	30.8	0.01748
0.5839	33.7	0.01733

WHITE LEAD (DRY), METALLIC LEAD DETERMINED AS ABOVE.

Sample.	1. Per cent.	2. Per cent.	3. Per cent.
A .....	79.3	79.2	79.0
B .....	78.9	78.7	...
C .....	79.5	79.8	79.5
D .....	79.0	78.9	...

WHITE LEAD GROUND IN OIL.<sup>1</sup>

Sample.	1. Per cent.	2. Per cent.	3. Per cent.
E .....	70.2	69.7	70.1
F .....	72.6	72.4	...

<sup>1</sup> In this case the sample should be dissolved in dilute nitric acid, boiled, filtered, solution neutralized with ammonia in excess, and then acidified with acetic acid in excess.



## LEAD BULLION.

Sample.	1. Per cent.	2. Per cent.
A.....	97.75	97.75
B.....	97.06	96.83
C.....	95.68	95.44
D .....	95.22	95.68

E, volumetric determination = 96.27 per cent.

E, gravimetric determination = 96.36 per cent. (from  $\text{PbSO}_4$ ).

ALLOY SAID TO CONTAIN LEAD EIGHTY PER CENT., ANTIMONY FIFTEEN PER CENT., AND TIN FIVE PER CENT.

Sample A (thoroughly oxidized), volumetric = 79.7 per cent., gravimetric = 79.79 per cent.

Sample B (thoroughly oxidized), volumetric = 80.6 per cent., gravimetric = 80.44 per cent.

Sample C (not completely oxidized), volumetric = 77.7-77.9 per cent., gravimetric = 75.56-75.41 per cent.

In using this method it will be found very convenient to employ the "equivalent weight" system, so that the percentage of metallic lead in the sample may be read directly upon the burette.

## MANUFACTURE OF PHOSPHOR BRONZE.

BY MAX H. WICKHORST.

Received March 18, 1897.

**P**HOSPHOR bronze is bronze containing a small amount of phosphorus, varying from a few hundredths of one per cent. to over one per cent. The phosphorus is added mainly to deoxidize the metal. It may be added to the bronze in substance as phosphorus, or in the form of a high phosphorus alloy.

At the brass foundry of the Chicago, Burlington & Quincy Railroad Company, at Aurora, Ill., we use the latter method. The alloy we call "hardener" and it contains six per cent. of phosphorus with copper and tin, in the ratio of 8 to 1.

*Manufacture.*—Our method of making this "hardener" is as follows: Ninety pounds of copper are melted in a No. 70 crucible (which holds about 200 pounds of metal when full), under charcoal, eleven pounds of tin are added, and the whole allowed

to become hot. The pot is then taken from the furnace and placed upon the floor. Then seven pounds of phosphorus are added in the following manner: A three-gallon stone jar half full of dilute solution of blue vitriol is weighed; phosphorus in sticks about four inches long is added until the weight is increased by seven pounds. The phosphorus remains in this solution half an hour or longer and is by this means given a coating of metallic copper, which prevents ignition when it is dried and exposed to the air. The phosphorus is then transferred from the vitriol solution to a pan (Fig. 1) to dry. The pan is made

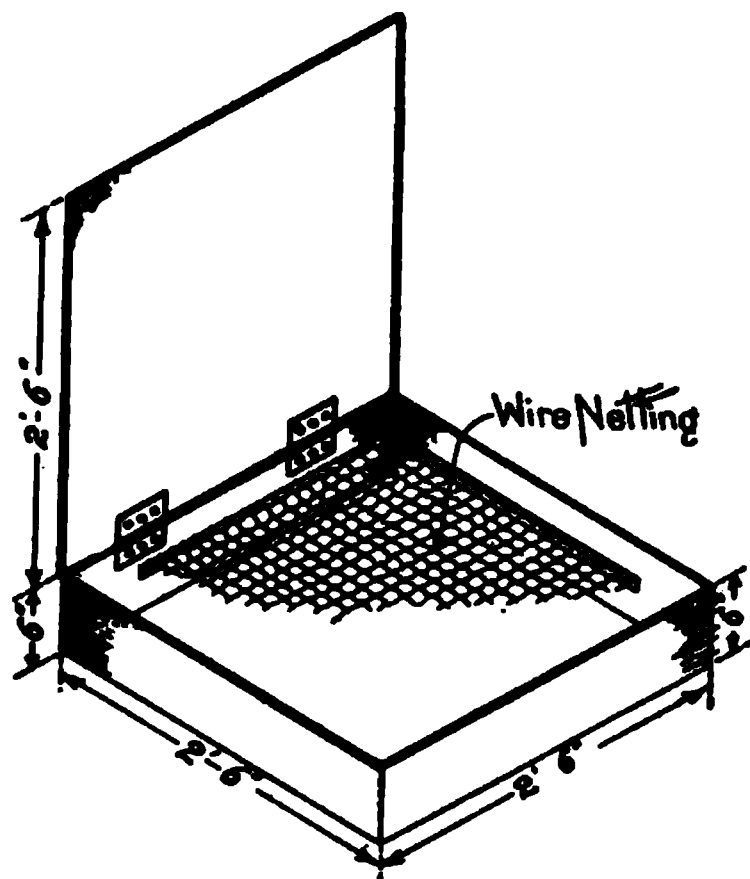


FIG. 1.

of galvanized iron about thirty inches square and six inches high. It contains about two inches of water. Over the water is wire netting supported from ledges along the inside of the pan. On the netting is blotting paper and on this the phosphorus is placed to dry. The pan has a lid which may be put down in case the phosphorus takes fire.

The phosphorus is introduced into the metal by means of a cup-shaped instrument called a retort or phosphorizer (Fig. 2), made of the same material as the graphite crucibles. The joint A is made tight with a cement of mineral paint mixed to a stiff paste with boiled oil. The metal having been melted and placed on the floor, one man holds the retort over the brim of the crucible, as shown in Fig. 2. Another workman takes

about three pieces of phosphorus and throws them into the retort. The first workman then immediately plunges the retort into the metal before the phosphorus can fall or flow out. The phosphorus of course immediately melts and begins to volatilize

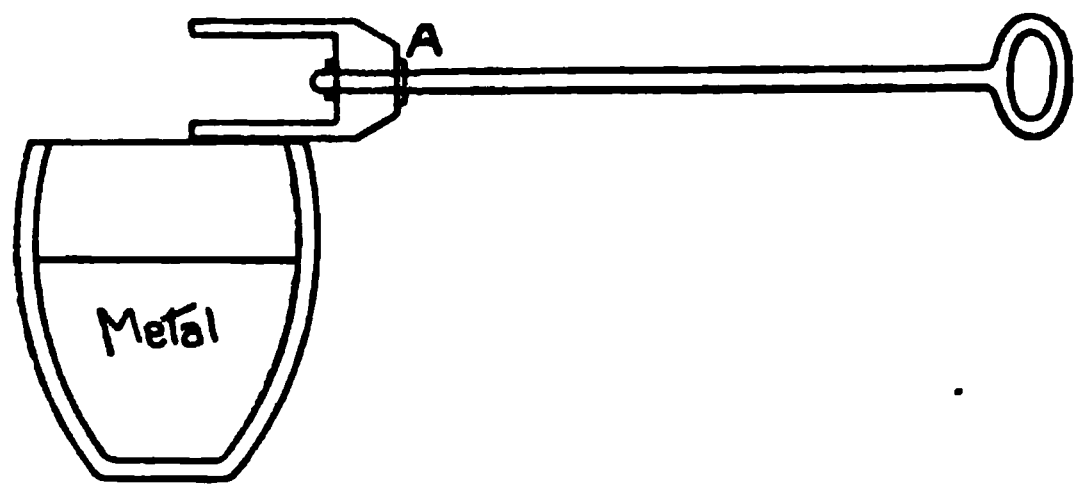


FIG. 2.

and as it comes in contact with the metal combines with it. This operation is repeated until the seven pounds of phosphorus have been added to the metal. Then the metal is poured into thin slabs about one inch by three inches by four inches. It is so hard that a greater thickness would make it difficult to break. Analysis shows this alloy to contain six per cent. of phosphorus. Ordinarily when we wish to add phosphorus to metal, we do it by adding a little of this high phosphorus alloy.

Our method of making phosphor bronze bearing metal is as follows :

COMPOSITION OF METAL.	
	Per cent.
Copper.....	79.7
Tin ....	10.0
Lead .....	10.0
Phosphorus .....	0.3
	<hr/>
	100.0

The copper is melted under charcoal, the tin and lead added, and enough "hardener" to get a sufficient amount of phosphorus.

Phosphorus has the effect of hardening bronze and it also makes it more fluid. The important property of phosphorus is however to deoxidize the metal, and it does this effectively.

# ANALYSIS OF PHOSPHOR BRONZE, PHOSPHOR COPPER, PHOSPHOR TIN, ETC.

BY MAX WICKHORST.

Received March 18, 1897.

*Determination of Phosphorus Alone.*—The following is a method which may be used where phosphorus alone is wanted, in phosphor bronze, phosphor copper, phosphor tin, etc.

Treat one gram of the sample with twenty cc. aqua regia, consisting of fifteen cc. nitric acid and five cc. hydrochloric acid and warm. When the reaction is complete, add water, then excess of ammonia, and make up to 200 cc. Pass in hydrogen sulphide until the copper, lead, etc., are all precipitated, and filter. To 100 cc. add ten cc. of magnesia mixture and ammonia in the usual manner. The phosphorus in the metal has been oxidized to the pentoxide by the aqua regia, and it is here obtained as the usual magnesium ammonium phosphate precipitate. After a few hours, filter off the precipitate into a Gooch crucible and wash with diluted ammonia water, containing a little ammonium sulphide. Dissolve the precipitate in a little dilute hydrochloric acid, add a little magnesia mixture and reprecipitate with ammonium hydroxide. Collect on a Gooch filter, ignite, and weigh. From this calculate the phosphorus. For most purposes the double precipitation may be dispensed with and the first precipitate ignited and weighed.

*Complete Analysis of Phosphor Bronze.*—Treat one-half gram of borings with five cc. of strong nitric acid, applying heat. After the reaction is over, rub the residue well with a rod, add a little water, filter off the residue on a nine cm. filter and wash with water containing a little nitric acid. Put the moist filter with contents into a weighed porcelain crucible, apply heat, at first very gently, and finally with a blast-lamp. The weight of the residue gives stannic oxide plus phosphorus pentoxide. Fuse the residue with one-half gram of sodium carbonate and one gram of sulphur, with cover on the crucible. Heat with Bunsen burner until excess of sulphur is all driven off. Allow to cool and dissolve the mass in hot water, add excess of ammonia, then one gram of ammonium chloride, and when cold precipitate with magnesia mixture. Collect the precipitate in the same manner as above, dissolve in a little dilute hydrochloric acid,

add ammonia and magnesia mixture, and re-collect and weigh the precipitate. This gives magnesium pyrophosphate, from which calculate phosphorus.

To obtain tin calculate magnesium pyrophosphate to phosphorus pentoxide, subtract this from stannic oxide plus phosphorus pentoxide. This gives stannic oxide. Calculate this to metallic tin.

However, by the treatment of the bronze with nitric acid, the phosphorus is not all rendered insoluble in combination with the tin. A little of it goes into the filtrate, and in order to get this phosphorus, a duplicate sample may be weighed out with the first, treated in the same way and filtered. The filtrate is precipitated with molybdate solution and the phosphorus determined in this by one of the usual methods. This phosphorus is added to that obtained above.

Frequently the tin and phosphorus are found together as above and the phosphorus determined in a separate portion of the sample. This is then calculated to phosphorus pentoxide, which is subtracted from the stannic oxide plus phosphorus pentoxide to give stannic oxide. But such a method causes results for tin a little too low, because, as explained above, the phosphorus is not all retained by the tin.

To the filtrate, from the stannic oxide plus phosphorus pentoxide, add ammonium hydroxide until just about neutral, then add five cc. nitric acid, make up to about 150 cc. with water, transfer to a large platinum dish and suspend in this a platinum foil about two inches square. Pass electric current through so as to precipitate the lead as dioxide on the dish, and the copper as metallic copper on the foil. Test whether action is complete by taking out a drop and treating with ammonia. If no blue color develops, the copper is all precipitated, and so also the lead, as its precipitation is complete long before all the copper has come down. Siphon off the liquid from the precipitates, pouring in fresh water meanwhile, until most of the acid is gone. Then disconnect the current and wash the precipitates well with water. Dry in an oven and weigh. This gives metallic copper direct, and the lead can be calculated from the lead dioxide.

The liquid may still contain iron and zinc. To determine these, warm the liquid somewhat, add an excess of ammonium

hydroxide and then ammonium sulphide. Allow to stand in a warm place until the precipitate has all settled, collect the precipitate on a small filter, ignite in a porcelain crucible, very cautiously at first, and finally with a blast-lamp. This gives ferric oxide and zinc oxide. Dissolve the ferric oxide and zinc oxide in hydrochloric acid, add water, heat, precipitate with ammonium hydroxide, collect ferric hydroxide, and calculate to metallic iron. Subtract ferric oxide from ferric oxide plus zinc oxide. This gives zinc oxide. Calculate to metallic zinc.

AURORA, ILL., MARCH, 1897.

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[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF THE U. S. DEPARTMENT OF AGRICULTURE, No. 26.]

## A NEW FORM OF CONDENSER FOR THE DISTILLATION OF LIQUIDS HAVING LOW BOILING-POINTS.

BY ERVIN E. EWELL.

Received March 17, 1897.

THE device to which I desire to call attention is one that will be of interest to all persons who find it necessary to distil large quantities of highly volatile liquids, during the warm months of the year. The apparatus is a comparatively simple one, consisting of a block-tin condensing worm surrounded by two copper jackets. Through the upper one of these, hydrant water is circulated for the preliminary cooling of the vapor; the lower one is filled with ice water for the complete condensation of the vapor and the thorough cooling of the distillate. In the apparatus that we have in use, this ice-water chamber is closed at the top and the ice water is prepared in a separate tank and allowed to flow into the jacket of the condenser at such a rate as the thermometer indicates to be necessary. Dr. Brown, formerly of this laboratory, has suggested that the ice-water chamber be made open and hopper-shaped at the top in order that the ice could fall directly into the cooling chamber. This action would doubtless lessen the amount of ice attention necessary for the satisfactory working of the apparatus. When chloroform or other liquids of moderately low boiling-points are being distilled, and during cold weather, the ice-water chamber is filled with water in both chambers.

The accompanying illustration shows the general form of the device for supporting it. A condenser

of this construction has been in use in this laboratory for nearly a year with perfect satisfaction. It has twenty-four turns of three-eighths inch block-tin piping in each chamber; the turns of the worm being two and one-half inches in diameter from cen-

ter to center of the pipe, each chamber has two hundred and twenty square inches of cooling surface.

The vessel containing the liquid to be distilled is placed upon a plate containing a small quantity of mercury. If the vessel is a beaker or of some other open form, it is covered with a bell-jar, which is connected with the condenser by means of an opening at the top; if the liquid is contained in a flask, direct connection is made with the condenser. The plate containing the mercury is heated by steam. For this method of arranging distilling vessels, see page 103, of Bulletin No. 28, Division of Chemistry, U. S. Department of Agriculture.

WASHINGTON, D. C., March 15, 1897.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY  
OF CALIFORNIA.]

## NOTES ON THE ESTIMATION OF CYANOGEN BY SILVER NITRATE, USING POTASSIUM IODIDE AND AMMO- NIA AS INDICATORS.<sup>1</sup>

BY WILLIAM J. SHARWOOD.

Received March 6, 1897.

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THE introduction of the "cyanide process" for extracting gold from its ores has given increased importance to the methods for determining cyanogen in alkaline cyanides. It is necessary to estimate rapidly the strength of the solutions used, and also of the spent solutions, in order to check losses and to show the amounts of additional cyanide requisite to fortify the spent liquors for further use.

The best known volumetric methods are those of Liebig (by titration with standard silver nitrate until a permanent precipitate forms) and of Fordos and Gelis (with standard iodine); that of Hannay (titration with standard mercuric chloride in

<sup>1</sup> The essential part of this paper was read before the Chemical Section of the Science Association of the University of California, March 30, 1896. A number of observations on the delicacy of indicator, and on oxidizing agents, have been added since.



presence of ammonia till precipitate is permanent) is open to objection as the end is indistinct in presence of many commonly occurring impurities. The iodine method requires the neutralization of free alkali, and Liebig's method has been most generally used, both on account of its simplicity and the permanence of the standard solution; it is, however, slightly affected by certain common interfering substances.

In the practical application of the "cyanide process," as usually carried out, the essential reactions are:

(I) For solution of the gold:



as was originally stated by Elsner, the necessity for the presence of free oxygen being disputed at first by MacArthur, but verified by MacLaurin.

(II) For precipitation by metallic zinc the equation usually given is:



Hence, starting with a solution of pure potassium cyanide, the spent liquors necessarily contain (beside the unaltered excess of potassium cyanide) potassium hydroxide, potassium zinc cyanide, and potassium zincate resulting from the solvent action of potassium hydrate upon zinc; the amount of zinc passing into solution is always far in excess of that calculated from the above equations on the basis of the gold precipitated. Owing to original impurities, to the decomposition of cyanide solutions in contact with the air, to incomplete precipitation, and especially to the action of various constituents of the ores treated (particularly sulphides in a more or less oxidized condition), there may also be present potassium aurous cyanide, potassium auric cyanide, potassium silver cyanide, mercuric cyanide, ferrocyanides, ferricyanides, double cyanides containing copper, nickel, or cobalt, (and probably manganese), cyanates, thiocyanates, sulphides, thiosulphates, ammonia compounds, oxamide, formates, etc., arsenites and antimonites (or their thio-salts), with sometimes very large quantities of calcium salts, and alkaline chlorides, sulphates, and carbonates. The potassium of commercial cyanide is often partly replaced by sodium, but without reducing its efficiency as a solvent for gold.

Caustic alkalies, alkaline plumbites, lime, soap, and certain oxidizing agents (as bromine, cyanogen bromide, mercuric chloride, and the peroxides of sodium and barium) are occasionally added during the process. The aim of the technical chemists has been primarily to estimate the simple alkaline cyanide, that existing in double cyanides having been considered "unavailable" for dissolving gold until recently, but certain double cyanides, especially that of zinc, have now been proved to have some solvent action.

Liebig's method gives accurately the cyanogen in solutions of alkaline cyanides, and of hydrocyanic acid after neutralization with soda or potash, the end-reaction consisting in a precipitation of silver cyanide; the addition of an alkaline chloride as indicator does not apparently affect the reaction. Cyanogen in mercuric cyanide, in cyanogen bromide, and in the double alkaline cyanides of silver, gold, nickel, cobalt, iron, copper, zinc, and a few other metals, cannot be estimated by it. Some of these substances, at least the two last mentioned metals, affect the determination of free alkaline cyanides to some extent. Solvents of silver cyanide, such as ammonia, ammonium carbonate, and thiosulphates, retard the end-reaction somewhat, giving high results; sulphides obscure it altogether by precipitating silver sulphide, and a large amount of free fixed alkali causes rather high results. Even in pure solutions the end is apt to be obscure or indefinite, a granular precipitate of silver cyanide forming and redissolving very slowly, making titration tedious. In presence of zinc (*i. e.*, pure potassium cyanide and pure potassium zinc cyanide) the end-reaction consists in the formation of a gelatinous precipitate of zinc cyanide soon after all the free or "available" alkaline cyanide has reacted. This "end" is rather vague, but is rendered sharper by addition of a little ferrocyanide as indicator, when a zinc ferrocyanide of doubtful composition falls out upon exhaustion of the uncombined alkaline cyanide; some of the cyanogen existing as double zinc cyanide is invariably reckoned in,<sup>1</sup> and this increases in presence of free alkali, so that the results of this so-called "available" cyanide

<sup>1</sup> Bettel (*Chem. News*, 72, 286, Dec. 13, 1895) states that exactly seven and nine-tenths per cent. of this is reckoned in. The writer has obtained variable results, averaging somewhat lower. Bettel himself mentions the time-effect and personal equation introduced.

titration are not strictly accurate. If enough caustic soda or potash be added to convert all zinc present into zincate *all* the cyanogen in the double zinc cyanide can be estimated ; but the end is not sharp and the excess of alkali modifies results appreciably. In practice a little ammonia may be present, retarding the end-reaction ; Mr. MacArthur appears to have been the first to suggest the use of potassium iodide as an indicator, the final precipitate being silver iodide, not appreciably affected by ammonia. Even with these improvements the end is not sharp and a precipitate is apt to form before reaction is complete, while time is a decided factor in titration when much zinc is present. The interference of soluble sulphides can be obviated by the method proposed by MacArthur, both for the estimation of cyanogen and as a metallurgical process, of adding lead carbonate or a solution of an alkaline plumbite and filtering off the lead sulphide formed.

In December, 1893, M. Georges Denigès<sup>1</sup> published a method of volumetrically estimating silver in any compound. He pointed out that none of the hitherto used volumetric processes for silver were universally applicable ; that Volhard's method with standard thiocyanate, though more general than Gay-Lussac's or Mohr's, could not be used with chlorides, bromides, or iodides of silver. He showed that every silver compound could be dissolved by means of potassium cyanide, or of ammonia and potassium cyanide (after a previous oxidation with nitric acid in the case of the metal, sulphide, and arsenide), without loss of cyanogen. He proposed to use a measured volume of a solution of potassium cyanide, in some excess of that required to form potassium silver cyanide with all the silver present, add ammonia and potassium iodide, and titrate with decinormal silver nitrate until a faint cloud of silver iodide forms ; then to titrate similarly an equal volume of the same cyanide solution with addition of ammonia and iodide ; the difference in the amounts of actual silver used in the two titrations equals the amount in the substance taken. The results quoted are perfectly concordant and accurate.

The present writer made at that time a few determinations of silver by this method, obtaining fair results, though less accu-

<sup>1</sup> *Compt. rend.*, 117, (26), 1078.

rate than with thiocyanate. Very satisfactory results were obtained in estimating iodide in presence of chloride, by precipitating with silver nitrate, treating with an excess of ammonia, washing the residue and redissolving it with potassium cyanide for titration. Some time later when estimating cyanogen by the method of Liebig, it struck the writer that an obvious corollary to Denigès' method for silver would be to apply his indicator, potassium iodide with addition of ammonia, to the determination of cyanogen; this was tried and very satisfactory results were obtained. The principal advantage found was in the rapidity of titration, the temporary precipitates dissolved instantly on shaking and the end was very sharp. In presence of zinc it was useless to attempt to determine "available cyanide;" increasing the ammonia indicated nearly all the cyanogen in potassium zinc cyanide, but never quite all unless fixed alkali were added. A number of experiments were then made to determine the accuracy of the method under varying conditions, more especially to ascertain the effect of the substances likely to occur in the liquors obtained in the MacArthur-Forrest and similar processes. Shortly after these were commenced, a second paper was published by M. Denigès, entitled "*Une nouvelle methode cyanimétrique*,"<sup>1</sup> in which he recommends the use of the same indicator for estimating cyanides and quotes numerous experiments, mentioning that his attention was called to the use of an iodide indicator by a consideration of the relative thermal effects produced in precipitating silver as iodide and as cyanide. M. Denigès has therefore priority in the use of this indicator, his improvement consisting in the deliberate introduction of ammonia as well as an iodide. As the results published by Denigès covered but few of the substances occurring in spent cyanide solutions, these experiments were continued by the writer and a number of the results are here given. Many of the salts (such as those of the organic acids) were used merely with a view to their possible use in correcting the effect of other interfering substances more likely to be met with.

Regarding the solutions used: that of potassium cyanide was of approximately one-fifth normal strength, prepared from the "ninety-eight per cent." commercial cyanide of German make,

<sup>1</sup> *Ann. chim. phys.*, [7], 6, 381.

an analysis of which is given. Several liters of decinormal silver nitrate were prepared and the same solution was used through about half the experiments; later a twentieth-normal solution was found to be preferable, on account of the delicacy of the end-reaction. The silver solutions were prepared from metal 998.6 fine and were very carefully standardized by Volhard's method, and adjusted to the strength indicated by comparison with the purest silver obtainable.<sup>1</sup> The standard of the silver solutions was assumed not to vary during the experiments; actually a change of nearly one-tenth per cent. was found after several months, the solutions being kept in the dark. Potassium iodide was used in a five per cent. or three-tenths normal solution; two cc., containing one-tenth gram, were commonly taken. Commercial ammonia was used, of sp. gr. 0.93, corresponding to ten times normal strength; occasional determinations showed it to vary from ten to nine and one-half times normal strength; three to five cc. were usually added.

The burette used for the standard silver solution had a capacity of fifty cc. and was graduated to tenths; the back was white with dark stripe, enabling it to be read to one-fortieth cc., but ordinarily it was read to one-twentieth. The quantities of cyanide solution used were so adjusted as to require, normally, about twenty cc. of solution; they were always measured with the same pipettes, of ten and twenty cc. capacity. The burette was tested, and the errors in the first twenty cc. were found to be quite negligible; before each determination it was refilled, so as to obtain a reading from zero to about twenty cc., except in a few cases. The ordinary error of observation could not thus exceed one part in 400, and was more nearly one in 800. The glass stop-cock gave a drop slightly exceeding one-thirtieth cc., so that an extra drop would correspond to one part in about 600 of cyanogen present. The apparently greasy condition of the inner surface of the burette, which follows some days' use, was found to be completely remedied (after use with silver nitrate) by rinsing with a little weak solution of potassium cyanide.

The temperature of the laboratory ranged from 16° to 21° C.

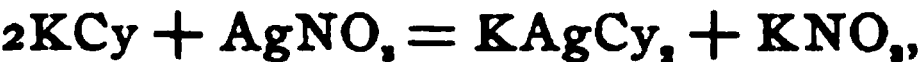
<sup>1</sup> This pure silver was prepared by reduction of fused chloride by pure zinc, and fusion of the washed metal, first with potassium bisulphate and then with borax; the chloride had been obtained by dissolving silver of a fineness of 998.6 in dilute nitric acid, filtering off the gold, precipitating from hot and highly dilute solution by hydrochloric acid, and repeatedly washing with hot water.

during observations, on only one or two occasions being 1° above or below these limits.

REACTIONS INVOLVED.

The reactions involved in the estimation of cyanogen by silver nitrate are :

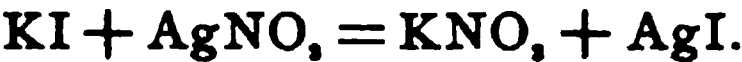
(1) Saturation, forming double silver cyanide :



and (2) precipitation of the excess of silver as *cyanide* :



or (3) as *iodide*, if an alkaline iodide be present :



The second reaction, but not the latter, being prevented by the presence of ammonium hydroxide or carbonate.

The terms "atom," "molecule," and "equivalent," as used in this paper in allusion to quantities of materials, refer to the corresponding weights expressed in *tenths of milligrams*, thus one cc. of tenth-normal silver nitrate contains one molecule silver nitrate, and corresponds in titration to two equivalents of cyanogen.

ANALYSIS OF "POTASSIUM CYANIDE 98 PER CENT."

	Per cent.	Corresponding to
Cyanogen.....	39.36	98.49 per cent. KCy.
Potassium .....	44.246	73.7 per cent. KCy.
Sodium .....	11.661	
Carbonic acid radical (CO <sub>2</sub> )..	3.57	6.31 per cent. Na <sub>2</sub> CO <sub>3</sub> .
Total determined.....	98.837	

Traces of chloride, sulphate and ammonia were found, and a little water, but no indications of thiocyanates, cyanates, nor of iron in any form.

The association of base and acid was calculated as a check on the analysis, all the alkali-metal not combined being reckoned as hydroxide.

	Per cent.
Potassium cyanide.....	73.7
Sodium cyanide .....	18.68
Sodium carbonate .....	6.31
Sodium hydroxide.....	0.25
	<hr/> 98.94

As the alkaline cyanides are about equally efficient as solvents of gold, it is customary to report analyses as "percentage of potassium cyanide," based merely on the estimation of cyanogen; this is often misleading, a great part of the potassium being frequently replaced by sodium, as in the above case, so that nominally "100 per cent." potassium cyanide may contain ten or twenty per cent. of impurity; in fact pure sodium cyanide would be reported as 133 per cent. potassium cyanide, and a mixture of one gram-molecule each of sodium and potassium cyanides with sixteen grams of impurity would yield apparently 100 per cent. potassium cyanide, while containing over twelve per cent. of impurity. It would seem desirable to report the valuation of cyanides in terms of the "cyanogen contained in alkaline cyanides," or in some similar manner.

**SERIES I.—COMPARISON OF RESULTS OBTAINED IN TITRATING POTASSIUM CYANIDE SOLUTIONS WITH STANDARD SILVER NITRATE BY THE METHODS OF LIEBIG AND DENIGÈS.**

In each case the same (one-fifth normal) solution of potassium cyanide was used; in using Denigès' method five cc. of decinormal ammonia were added and one decigram of potassium iodide; each was titrated with silver nitrate of decinormal strength.

*Set I.*—By Liebig's method:

(a)	20	cc.	potassium cyanide solution required	19.65	cc.	silver nitrate.
(b)	20	"	" " " "	19.7	"	" "
(c)	20	"	" " " "	19.65	"	" "

Mean 19.667 " " "

*Set II.*—By the method of Denigès:

(d)	20	cc.	potassium cyanide solution required	19.7	cc.	silver nitrate.
(e)	20	"	" " " "	19.7	"	" "
(f)	40	"	" " " "	39.35	"	" " or
(g)	20	"	" " " "	19.675	"	" "

Mean 19.692 " " "

**SERIES 2.—EFFECT OF VARYING VOLUME OF SOLUTION.**

Using twenty cc. fifth-normal potassium cyanide solution, five

cc. ammonia, and one-tenth gram potassium iodide and adding water to make final volume 50 cc. or 150 cc.

(a)	20 cc.	diluted to 50 cc.	required	19.70 cc.	tenth-normal silver nitrate.
(b)	20 cc.	"	50 "	"	19.70 "
(c)	20 cc.	"	150 "	"	19.75 "
(d)	20 cc.	"	150 "	"	19.70 "

SERIES 3.—PROPORTIONALITY OF SILVER NITRATE USED TO  
CYANIDE PRESENT.

The potassium cyanide was added from a ten cc. pipette. Three cc. ammonia and one-tenth gram potassium iodide were used.

10 cc.	potassium cyanide solution required	9.8 cc.	silver nitrate.
20 "	"	19.6 "	"
30 "	"	29.4 "	"

SERIES 4.—EFFECT OF VARYING THE PROPORTIONS OF THE  
INDICATORS : POTASSIUM IODIDE AND AMMONIA.

The ammonia water was of approximately ten times normal strength.

*Set I.*—Varying potassium iodide, ammonia constant ; using twenty cc. fifth-normal potassium cyanide, and five cc. ammonia.

Grams potassium iodide added.....	0.05	0.1	0.25	0.5
cc. tenth-normal silver nitrate required.	19.7	19.7	19.75	19.7
"	19.75	19.7	....	19.7
"	19.7	19.75	....	19.7
"	....	19.7	....	....

*Set II.*—Varying both ammonia and potassium iodide. Using twenty cc. fifth-normal potassium iodide solution at a temperature of about 20° C.

Grams potassium iodide added.....	0.1	0.5	0.5	0.5
cc. ammonia added.	cc. tenth-normal silver nitrate required.			
5 .....	19.7	19.75	19.7	19.7
10 .....	...	19.8	...	19.75
20 .....	...	...	...	19.85
30 .....	...	...	...	19.9
55 .....	20.2	20.1	...	...

*Set III.*—Using ten cc. of another fifth-normal solution of potassium cyanide at a temperature of 14° C.



Grams potassium iodide added.....	0.1	0.1	0.25	1.0
cc. ammonia added.	cc. twentieth-normal silver nitrate required.			
0 .....	20.02	20.05	20.05	....
2 .....	....	....	....	20.15
5 .....	20.05	20.05	....	....
15 .....	....	....	20.1	....
20 .....	20.13	20.18	....	....
30 .....	20.25	....	....	....
40 .....	....	....	....	20.25
50 .....	20.5	20.55	....	20.25

#### SERIES 5.—EFFECT OF VARYING TEMPERATURE.

*Set I.*—Using twenty cc. fifth-normal potassium cyanide solution, five cc. ammonia, and one-tenth gram potassium iodide.

Temperature .....	22°	45°	72°
cc. decinormal silver nitrate required	19.7	19.85	20.0

*Set II.*—Varying temperature and varying ammonia. Using ten cc. fifth-normal potassium cyanide and one-tenth gram potassium iodide, titrating with twentieth-normal silver nitrate.

Temperature.....	20°	48°	80°
cc. of tenth-normal ammonia added.	cc. tenth-normal silver nitrate added.		
5 .....	(a) 20.05	(a) 20.2	(a) 20.3
5 .....	(b) 20.05	...	...
15 .....	(b) 20.1	. .	(b) 20.8
20 .....	...	...	(b) 21.1

In the last set of experiments the solution was warmed, or ammonia added, or both, until the end-precipitate from one determination had redissolved; silver nitrate was then added, drop by drop, until the precipitate reappeared.

From the preceding figures it seems that moderate variations in the proportions of indicators have but little effect on the results of estimating cyanogen by this method; it is, however, evidently desirable to keep the temperature constant, and to avoid an undue excess of ammonia which gives results somewhat too high.

In presence of a large amount of ammonia the error may be reduced somewhat by adding a larger amount of potassium iodide, but under ordinary conditions one-tenth gram is sufficient.

#### SERIES 6.—DELICACY OF INDICATOR.

*Set I.*—(a) With five cc. ammonia and one-tenth gram potas-

sium iodide, in fifty cc. water, no cyanide being added, one drop (or 0.03 cc.) of twentieth-normal silver nitrate was sufficient to give a very decided cloud of silver iodide. Using the same quantities of ammonia and iodide in 150 cc. of water, the same amount of silver salt gave a decided cloud, though of course less dense than in the smaller volume of liquid.

(*b*) With fifty cc. of a very dilute solution of sodium chloride, and adding five cc. ammonia and one-tenth gram potassium iodide, one drop of twentieth-normal silver nitrate gave a similar precipitate. In a similar solution, without these indicators, three to four drops were necessary to give an equally dense cloud.

(*c*) Taking forty cc. of a ten per cent. solution of sodium chloride, one drop of twentieth-normal silver nitrate gave a precipitate as heavy as in the preceding case, when ammonia and iodide were added. In an equal amount, without the indicator, three drops were necessary to give a permanent cloud, and four or five to render it as heavy as with the indicator.

(*d*) So also in forty cc. of a five per cent. solution of ammonium chloride, with ammonia and iodide, one drop of twentieth-normal silver nitrate gave a similar cloud; without the indicator, one drop gave a faint opalescence, two gave about the same effect as one gave with iodide present.

Owing to the fact that no permanent precipitate is formed in presence of the slightest excess of alkaline cyanides, it was impossible to strictly compare the delicacy of the end-reaction with and without the iodide indicator. As the difference seemed to lie rather in the colors than in the solubilities of silver iodide and cyanide, it was thought that a comparison of the iodide and chloride might give approximately the same results. The following tests were all made with fifty cc. of distilled water, in flasks of about 120 cc. capacity.

*Set II.*

	Amounts present.			Silver nitrate solution added. (Twentieth normal from burette.)	Effects of silver added.
	Sodium chloride. Gram.	Potassium iodide. Gram.	Ammonia. cc.		
( <i>a</i> )	0.1	0.1	3	1 drop (0.035)	Decided cloud.
( <i>b</i> )	0.1	0.1	0	1 "	Cloud, slightly less dense than in ( <i>a</i> ).
( <i>c</i> )	0.1	0.0	0	1 "	Opalescence.
				2 "	Cloud, as dense as ( <i>a</i> ).

*Set III.*

	Amounts present.			Silver nitrate solution added.	Effects of silver added.
	Sodium chloride. Gram.	Potassium iodide. Gram.	Ammonia. cc.	(One-hundredth normal from Mohr pipette.)	
(a)	0.1	0.1	3	0.1 cc.	Slight opalescence.
				0.2 "	Decided "
(b)	0.1	0.1	0	0.13 "	Faint "
				0.2 "	Decided "
(c)	0.1	0.0	0	0.1 "	Very faint "
				0.6 "	Precipitate equal in opacity to (a) with 0.2 cc.

*Set IV.*

(a)	0.1	0.1	3	0.12 cc.	Decided opalescence.
(b)	0.1	0.1	0	0.22 "	" " equal to (a).
(c)	0.1	0.0	0	0.15 "	Faint opalescence.
				0.29 to 0.35 cc.	" " equal to (a).

*Set V.*

(a)	0.1	0.1	3	1 drop (0.04 cc.)	Opalescence, slightly more than in (c) with one drop.
				2 "	Opalescence greatly increased.
(b)	0.1	0.1	0	1 "	Opalescence less than (a) or (b) with one drop.
				2 "	Opalescence increased, much less than (a) but more than in (c) with second drop.
				4 "	Opalescence equal to (a) with two drops.
(c)	0.1	0.0	0	1 "	Opalescence.
				2 "	" very slightly increased.
				6 "	Opalescence almost equal to (a) with two drops.

*Set VI.*—Identical with V, but made in reverse order.

Sets II, III, and IV were carried out in diffused light on a rather dull day; sets V and VI on a bright day, the flasks being held momentarily in direct sunlight for comparison. As

the appearance varies slightly with time, Set V was repeated in reverse order (VI), but the results did not apparently differ. In sets V and VI the effect of time was closely noticed; after standing five minutes the precipitate in (a), at first practically equal to the others, was appreciably heavier; after ten minutes that in (c) was evidently increasing; after one and two hours that in (c) was by far the most dense, (b) next, and (a) somewhat less dense than (b), proportionally to the amount of silver nitrate added to each.

It seems remarkable that the addition of ammonia should increase the delicacy of the iodide precipitation of silver, but the results in all the last five sets of tests indicate that this is the case, at least within a few minutes of the precipitation, the time when the sensitiveness of an end-reaction is of most value. The addition of ammonia has therefore the unexpected advantage of rendering the end still sharper than it is with potassium iodide alone, as well as of redissolving the temporary precipitates more rapidly than the cyanide does when nearing the end of titration, while the use of the simple iodide indicator is preferable to the ordinary "Liebig" method, chiefly on account of the yellowish color of the silver precipitate, this being more readily visible than silver chloride or cyanide, either with a dark or light background.

*Effect of Indicator in Presence of Considerable Proportions of Alkaline Ferrocyanides, Ferricyanides, Thiocyanates, and Thiosulphates.*

As the above salts in quantity caused some variation in the amounts of cyanide found by titration, the following tests were made with a very dilute (one hundredth-normal) solution of silver nitrate, to ascertain the extent to which they dissolved silver iodide, and the readiness with which they themselves precipitated silver from the nitrate.

*Set VII.*—The volume of liquid was in each originally twenty-five cc., no cyanide being taken.

Salt taken.	NH <sub>4</sub> CNS.	K <sub>4</sub> FeCy <sub>6</sub> .	K <sub>3</sub> FeCy <sub>6</sub> .
Grams of salt added (crystals) .....	1.9	1.09	0.825
Molecules " " " .....	250.0	25.0	25.0

cc. hundredth-normal silver nitrate required to precipitate :

(a) With one-tenth gram potassium iodide and three cc. ammonia as indicator .....	0.85	0.75	0.4
(b) Without indicator.....	{ over 10.0 <sup>1</sup>	1.0	about 0.5
Equivalents of cyanogen corresponding to silver used with iodide indicator.....	0.17	0.15	0.08
Molecules potassium cyanide to give same effect as one molecule of salt, with indicator.....	0.0007	0.006	0.003

*Set VIII.*—Using one-tenth gram of crystallized sodium thiosulphate (4 molecules) in twenty-five cc. water, no cyanide being added.

	(a)	(b)	(c)	(d)
Indicator used.....	none.	0.1 gr. NaCl.	0.1 gr. KI.	0.1 gr. KI+3 cc. NH <sub>4</sub> OH.
cc. twentieth-normal silver nitrate required to give a precipitate .....	over 10; (solution blackens.)	6.4	0.15	0.1
Molecules potassium cyanide to give same effect as one molecule sodium thiosulphate .....	?	1.6	0.04	0.025
Molecules sodium thiosulphate to give same effect as one molecule potassium cyanide .....	?	0.625	27.0	40.0

The use of ammonia and iodide as an indicator is therefore of great advantage in presence of thiocyanates and thiosulphates, but of only slight advantage in presence of ferrocyanides, and makes little difference with ferricyanides.

#### SERIES 7.—EFFECT OF FIXED CAUSTIC ALKALI.

*Set I.*—Using twenty cc. fifth-normal potassium cyanide solution, five cc. ammonia and one-tenth gram potassium iodide :

cc. of two per cent. solution of sodium hydroxide added .....	0.0	50.0	100.0
cc. of tenth-normal silver nitrate solution required .....	19.7	19.7	19.7

Further additions of 50 and 100 cc. of soda solution did not appreciably affect precipitate.

*Set II.*—Using five cc. fifth-normal potassium cyanide, added to forty cc. water.

<sup>1</sup> Required 12.3 cc. of twentieth-normal.

Potassium hydroxide added.....	none	4 grams
		cc. twentieth-normal silver nitrate required.
(a) By Liebig's method, without indicator .....	9.75	10.9
(b) By Denigès' method, with three cc. ammonia and one- tenth gram potassium iodide.....	9.75	9.8

A more extended series of comparisons is quoted by Denigès.

SERIES 8.—EFFECTS OF VARIOUS SALTS.

In these determinations the salts were either weighed out directly, dissolved and added, or were measured out from roughly standardized solutions. Approximately fifth-normal potassium cyanide solution was used, ten cc. being usually taken, with three or five cc. ammonia, and one-tenth gram potassium iodide as indicator. The approximate numbers of molecules of each salt, associated with twenty molecules of potassium cyanide, is given in column 3. The numbers of equivalents of cyanogen, given in columns 4 and 5, were taken as equal to the numbers of cc. of twentieth-normal silver nitrate consumed, those of column 4 being daily checked.

Substance added.	Grams.	Molecules.	Equivalents of KCy taken.	Equivalents of Cy found by titration.	Difference.	Percentage error.
Sodium chloride.....	2.4	400.0	20.0	19.9	0.1	+0.5
" " .....	4.0	680.0	19.8	19.85	0.05	+0.25
" " .....	4.0	680.0	19.8	19.8	0.0	0.0
Sodium sulphate (cryst).	6.5	200.0	20.0	0.0	0.0	0.0
Sodium carbonate (cryst)	1.43	50.0	20.05	20.1	0.05	+0.25
Sodium carbonate (cryst. = 0.53 gram anhy- drous) .....	1.43	50.0	20.05	20.0	0.05	—0.25
Potassium nitrate.....	1.05	100.0	20.05	19.9	0.15	—0.75
" " .....	5.2	500.0	19.8	19.7	0.1	—0.5
Ammonium chloride....	1.2	220.0	20.0	19.8	0.2	—1.0
" " ....	1.8	330.0	19.8	19.8	0.0	0.0
" " ....	3.0	550.0	19.8	19.8	0.0	0.0
Disod. phosphate (cryst)	1.43	40.0	20.0	±20.0 <sup>1</sup>	±0.2	±1.0
Disod. phosphate (+0.5 gram NaOH).....	1.43	40.0	20.0	±20.0 <sup>1</sup>	±0.2	±1.0
Microcosmic salt.....	4.2	200.0	20.0	19.8	0.2	—1.0

## ESTIMATION OF CYANOGEN.

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Substance added.	Grams.	Molecules.	Equivalents of KCy taken.	Equivalents of Cy found by titration.	Difference.	Percentage error.
Sodium sulphite ( $7H_2O$ )	2.5	100.0	20.0	19.95	0.05	-0.25
Potassium chlorate.....	1.0	80.0	20.0	20.0	0.0	0.0
Potassium dichromate (titrated immediately).....	0.125	4.2	20.0	20.1	0.1	+0.5
Potassium dichromate (titrated after ten minutes).....	0.44	15.0	20.15	20.2	0.05	+0.25
Potassium dichromate (titrated after one hour).....	0.44	15.0	20.15	19.85	0.30	-1.5
Ammonium oxalate .....	1.07	75.0	20.0	20.0	0.0	0.0
Sodium formate.....	2.75	320.0	20.0	20.0 <sup>1</sup> to 20.05	0.0 to +0.05	0.0 to +0.25
Acetic acid (glacial, neu- tralized by soda).....	3.0	500.0	20.0	19.9	0.1	-0.5
Citric acid (neutralized by soda).....	3.0	140.0	20.0	20.0	0.0	0.0
Tartaric acid (neutralized by soda).....	3.0	250.0	20.0	20.0	0.0	0.0
Arsenious oxide (+excess NaOH) .....	0.132	7.0	20.0	20.1	0.1	+0.5
Arsenious oxide(+excess NaOH) .....	0.132	7.0	20.0	20.15	0.15	+0.75
Sodium arsenite ( $Na_2H-$ $AsO_3$ , anhydrous).....	1.0	0.0	20.0	20.05	0.05	+0.25
Potassium antimonite ...	2.0	...	19.8	19.8 to 19.9	0.5 to 0.1	+0.25 to +0.5
Potassium stannate .....	2.0	...	19.8	19.85	0.05	+0.25
Sodium plumbite (Pb 0.105 gram) .....	..	5.0	19.8	19.5	0.3	-1.5
Sodium plumbite (Pb 0.105 gram + excess NaOH) .....	..	5.0	19.8	19.7	0.1	-0.5
Sodium plumbite (Pb 0.207 gram + excess NaOH) .....	..	10.0	19.8	19.7	0.1	-0.5
Sodium silicate.....	2.0	...	19.8	19.7 <sup>1</sup>	0.1	-0.5
Borax.....	4.0	100.0	10.05	10.05	0.0	0.0
Barium chloride (cryst.)	1.85	75.0	19.8	19.75-19.85	$\pm 0.05$	$\pm 0.25$
Calcium chloride(anhyd)	2.78	250.0	20.0	19.95-20.05	$\pm 0.05$	$\pm 0.25$

<sup>1</sup> End not sharp.

Substance added.	Grams.	Molecules.	Equivalents of KCy taken.	Equivalents of Cy found by titration.	Difference.	Percentage error.
Potassium alum.....	2.8	60	20.0	19.95	0.05	-0.25
(with sodium hydroxide).....	(0.32)	(80)				
Chrome alum (with sodium hydroxide)....	0.25	5.0	16.0	16.05	0.05	+0.3
Chrome alum (with sodium hydroxide)....	3.0	60.0	19.8	19.2	0.6	-3.0
Magnesium sulphate crystals, with ammonium chloride.	2.0	80.0	20.05	20.1	0.05	+0.25
	0.36	66.0				
Ammonium thiocyanate.	0.152	20.0	19.7	19.6	0.1	-0.5
" "	0.152	20.0	19.8	19.7	0.1	-0.5
" "	0.152	20.0	19.8	19.75	0.05	-0.25
" "	1.6	200.0	19.8	19.8	0.0	0.0
" "	1.6	200.0	19.8	19.85	0.05	+0.25
Potassium ferrocyanide..	0.17	4.0	39.4	39.5	0.1	+0.25
" "	2.18	50.0	19.8	19.9	0.1	+0.5
" "	2.18	50.0	19.8	19.9	0.1	+0.5
" "	2.18	50.0	10.05	10.15	0.1	+1.0
Potassium ferricyanide..	0.132	4.0	19.7	19.7	0.0	0.0
Potassium ferricyanide (solution two weeks old) .....	0.658	20.0	20.15	19.2	0.95	-4.9
Potassium ferricyanide (new).....	0.658	20.0	20.15	20.0	0.15	-0.75
Potassium ferricyanide (new with NaOH) .	0.658	20.0	20.15	19.6	0.55	-2.7
				to 19.9	to 0.25	to -1.25
Potassium ferricyanide (new with NaOH).	0.658	20.0	10.05	9.95	0.1	-1.0
Sodium thiosulphate....	0.25	10.0	20.1	20.95	0.85	+4.2
Sodium thiosulphate....	0.5	20.0	20.1	21.8	1.7	+8.5
Alcohol (50 cc., pure 50 per cent.).....	..	...	20.1	20.1	0.0	0.0
Alcohol (100 cc., commercial 50 per cent.) ....	..	...	20.1	20.3	0.2	+1.0
Cane sugar .....	5.0	...	19.8	19.8	0.0	0.0
Soap.....	0.25	...	19.8 <sup>1</sup>	19.75-19.85	±0.05	±0.25

It will be seen that relatively large proportions of salts were

<sup>1</sup> End not sharp.



added in most of the experiments quoted: numerous other experiments were made with smaller quantities, the effects of which were generally quite negligible. The effects of oxidizing agents, and of salts of metals forming double cyanides (generally proportional to the amounts added), and of thiosulphates and sulphides, are given in other series. Nitrates generally give somewhat low results. Salts of aluminum, chromium, and magnesium interfered greatly unless kept in solution by fixed alkali or sal ammoniac respectively. With chromium the end-reaction can be clearly seen by looking through a thin layer of the green liquid at a white object. Calcium salts render the end indistinct by precipitating as carbonates; this is partially remedied by sal ammoniac. Iron salts gave precipitates when added, and the results of subsequent titration were most irregular; attempts were made to retain the iron in solution by addition of organic acids, followed by excess of alkali; in some instances this was entirely successful, but generally the results were low and variable, and were not thought worth tabulating.

The stannates and salts of their class were studied with a view to their possible use to prevent the interference of sulphides; they generally give somewhat high results, while those with plumbites are a trifle low. In presence of phosphates the end is somewhat uncertain, and similarly with large proportions of sodium carbonate and chloride; such solutions should be diluted and the silver solution added slowly.

Moderate additions of thiocyanates gave slightly low results; with very large amounts, results are normal or very slightly high. Ferrocyanides gave rather high results, the percentage error increasing fairly regularly with the ratio of ferrocyanide to simple cyanide. With ferricyanides the results were low, but irregularly low; additions of ammonia or fixed alkali seemed rather to increase the irregularity; time affected the interference of ferricyanides, and the final precipitate increased greatly on standing. The interference of small proportions of the three last-mentioned salts,<sup>1</sup> such as met in working solutions, would be ordinarily negligible. Their effect on the indicator is shown in series 6, set VII, that of thiosulphates in set VIII.

<sup>1</sup> For a discussion of the interference of these salts with the iodine and Liebig methods of titration, see J. E. Clennell, *Chem. News*, 5, 72, 1882.

SERIES 9.—EFFECTS OF ZINC.

The zinc was added in the form of a solution of the chloride, containing 0.0099 gram metal per cc. (1 cc. = 1.52 atoms zinc).

The series of results, indicated in any vertical column, were obtained by adding ammonia (or, in some cases, sodium hydroxide or ammonium chloride) in sufficient quantity to redissolve the precipitates formed, and then continuing the titration until a further precipitation occurred.

*Effect of Varying Zinc and Ammonia.*

*Set I.*—Using twenty cc. fifth-normal potassium cyanide solution (containing 39.4 equivalents Cy), and one-tenth gram potassium iodide.

Zinc added—grams		0.0	0.0198	0.0495	0.099		
Zinc added—atoms		0.0	3.04	7.6	15.2		
Ammonia added, ten times normal.			cc. tenth-normal silver nitrate required.				
cc.	(Mols.)	*	Diff.		Diff.		Diff.
5	(500)	19.7	18.8	(0.9)	16.85	(2.85)	12.65 (7.05)
10	(1000)	19.75	19.3	(0.45)	18.15	(1.6)	16.3 (3.45)
15	(1500)	19.8	19.45	(0.35)	18.7	(1.1)	17.55 (2.25)
20	(2000)	19.85	same		19.0	(0.85)	18.2 (1.65)
25	(2500)	19.9	....		19.2	(0.7)	18.6 (1.3)
30	(3000)	19.95	....		same		18.8 (1.15)
35	(3500)	20.0	....		....		19.0 (1.0)
40	(4000)	20.5	....		....		same

*Set II.*—Using ten cc. fifth-normal potassium cyanide solution (containing 20.05 equivalent Cy), and one-tenth gram potassium iodide, adding 0.0297 gram zinc (4.56 atoms) in each case.

Ammonia added, ten times normal.			cc. tenth-normal silver nitrate required.	Differ- ence from 10.03
cc.	(Mols.)			
1	(100)		1.15	(8.88)
3	(300)		8.55	(1.48)
5	(500)		9.0	(1.03)
7	(700)		9.25	(0.78)
9	(900)		9.5	(0.53)
11	(1100)		9.6	(0.43)
11	(1100) + 0.08 gram NaOH = 20 molecules		9.8	(0.23)
11	(1100) + 0.16 gram NaOH = 40 molecules		9.95	(0.08)

Throughout the series of experiments with zinc and ammonia the precipitates (which appeared to consist of zinc cyanide)

\* Some of the numbers in this column were obtained by interpolation.

redissolved on standing a short time; the titrations were therefore performed by adding the silver nitrate solution drop by drop, increasing the interval to about a quarter of a minute as the "end" approached; the numbers given indicate the least volumes which gave a precipitate that was permanent for about a minute.

*Effects of Zinc in Presence of Ammonium Chloride and Ammonia.*

*Set III.*—Using ten cc. fifth-normal potassium cyanide solution (containing 20.05 equivalents Cy), and one-tenth gram potassium iodide, adding 0.0297 gram zinc (4.56 atoms) in each case.

Ammonia added, ten times normal. cc. (Mols.)	Ammonium chloride added. Gms. (Mols.)	cc. tenth-normal silver nitrate added.	Diff. from 10.03.
1 (100)	0.6 (110)	3.5 slight precipitate, redissolves slowly.	(6.53)
1 (100)	0.6 (110)	4.0 " " " "	(6.03)
1 (100)	0.6 (110)	5.0 " " permanent two minutes.	(5.03)
3 (300)	1.2 (220)	8.5 " " " "	(1.53)
5 (500)	1.2 (220)	9.0 " " " "	(1.03)
7 (700)	1.2 (220)	9.3 " " permanent.	(0.73)

A comparison of the last two tables shows that ammonium chloride has but little effect in preventing the interference of zinc compounds, as compared with ammonia, while caustic soda is far more effective than either.

When little or no ammonia is added the number of equivalents of cyanogen, retained by one atom of zinc, approaches four, but never reaches it. The first additions of ammonia greatly reduce the ratio of cyanogen to zinc; larger additions have a less proportionate effect, but gradually bring the cyanogen combined by the zinc to near zero.

*Effect of Zinc in Presence of Caustic Soda.*

*Set. IV.*—Using in each case twenty cc. fifth-normal potassium cyanide solution, with varying amounts of zinc chloride and varying amounts of four-tenths normal solution of caustic soda, adding to each five cc. ammonia and one-tenth gram potassium iodide.

Zn added—grams	0.0	0.198	0.0495	0.099	0.198
Zn added—atoms	0.0	(3.0)	(7.6)	(15.2)	(30.4)
Sodium hy- droxide solu- tion added.					
cc. (Mols.)	Gms.	cc. tenth-normal silver nitrate required. Diff.	Diff.	Diff.	Diff.
0	0	19.8	18.85 (0.95)	16.9 (2.9)	12.4 (7.4)
10 (40)	19.8	19.75 (0.05)	19.7 (0.1)	17.5 (2.3)	8.85 (11.25)
20 (80)	19.8	....	19.8 (0.0)	19.5 (0.3)	15.1 (4.7)
30 (120)	19.8	....	...	19.6 (0.2)	19.4 (0.4)
40 (160)	19.8	....	...	...	19.6 (0.2)

Additions of caustic soda, further than those indicated, failed to redissolve the end-precipitate. It is evident that the interference of zinc is minimized when the number of molecules of caustic soda added exceeds four times the number of atoms of zinc present.

#### SERIES 10.—EFFECT OF COPPER.

Copper was added as a solution of the nitrate, containing 0.005 gram metal per cc. (1 cc. = 0.79 atom copper); 0.1 gram potassium iodide was added in each case.

#### *Varying Copper and Ammonia.*

*Set I.*—Using twenty cc. fifth-normal potassium cyanide solution containing 39.6 equivalents of cyanogen.

Copper added—grams	0	0.025	0.05	0.075
Copper added—atoms	0	3.95	7.9	11.85
Ammonia added ten times normal.				
cc. (Mols.)	Gms.	cc. tenth-normal silver nitrate required. Diff.	Diff.	Diff.
5 (500)	19.8	13.0 (6.8)	6.2 (13.6)	1.2 (18.6)
10 (1000)	19.85	13.2 (6.65)	6.55 (13.3)	1.2 (18.65)
15 (1500)	19.9	13.3 (6.6)	6.8 (13.1)	2.2 (17.7)
20 (2000)	19.95	13.4 (6.55)	7.05 (12.9)	2.65 (17.3)
25 (2500)	20.0	same	7.25 (12.75)	2.85 (17.15)
30 (3000)	20.05		same	3.15 (16.9)
Equivalents of cyanogen com- bined by one atom of copper		3.43 to 3.3,	3.43 to 3.22,	3.18 to 2.85.

Time affected results somewhat; the precipitates slowly cleared.

#### *Effect of Copper in the Presence of Caustic Soda.*

*Set II.*—Using twenty cc. of fifth-normal potassium cyanide solution (containing 39.6 equivalents Cy), with five cc. ammonia and one-tenth gram potassium iodide, adding 0.05 gram copper as nitrate (7.9 atoms copper).

Sodium hydroxide added.	cc. tenth-normal silver nitrate required.	Diff.
none	6.2	(13.6)
0.32 gram (80 mols.)	6.3 to 6.35	(13.5)

A temporary black precipitate formed on each addition of silver solution, rendering the end rather indistinct.

**SERIES 11.—EFFECT OF CADMIUM, VARYING CADMIUM AND AMMONIA.**

Cadmium was added as a solution of the nitrate, containing 0.03 gram metal per cubic centimeter (1 cc. = about 2.6 atoms cadmium).

Ten cc. fifth-normal potassium cyanide solution were used in each case, with one-tenth gram potassium iodide.

Cadmium added—grams		0	0.06	0.12	0.12*	0.3
Cadmium added—atoms		0	5.2	10.0	10.0	26.0
Ammonia added ten times normal.		cc. tenth-normal silver nitrate required.				
cc.	(Mols.)	Gms.	Diff.	Diff.	Diff.	Diff.
3	(300)	10.05	7.4 (2.65)	..	7.0 (3.05)	..
4	(400)	10.05		8.4 (1.65)	..	5.5 (4.55)
6	(600)	10.05	8.6 (1.35)	9.0 (1.05)	9.3 (0.75)	7.35 (2.70)
8	(800)	10.05				8.0 (2.05)
10	(1000)	10.05				8.7 (1.35)
14	(1400)	10.05				9.0 (1.05)
18	(1800)	10.05				9.5 (0.55)

The end-point was very indefinite in presence of cadmium; neither ammonium hydroxide nor the chloride affected the irregularity of the final precipitates, which sometimes slowly cleared and at other times greatly increased on standing. In several other experiments, with smaller amounts of cadmium, the interference was practically avoided by a considerable addition of ammonia. Caustic soda was without effect.

**SERIES 12.—INTERFERENCE OF VARIOUS METALS FORMING SOLUBLE DOUBLE CYANIDES.**

Metal.	Gram metal added.	Atoms metal added.	Equivalents KCy taken.	Equivalents Cy found by titration.	Difference (= equivalents of Cy combined).	Equivalents Cy combined per atom of metal.
Gold—as $\text{HAuCl}_4\text{Aq.}$ .....	0.018	0.914	25.0	21.1	3.9	4.27
as $\text{KAuCl}_4\text{Aq.}$ .....	0.018	0.914	25.0	21.3	3.7	4.05
as $\text{HAuCl}_4\text{Aq.}$ .....	0.09	4.57	39.4	20.6	18.8	4.11

\* Ammonium chloride (0.33 gram = 60 mols.) was added in this case.

Metal.	Gram metal added.	Atoms metal added.	Equivalents KCy taken.	Equivalents Cy found by titration.	Difference(=equiv- alents of Cy com- bined).	Equivalents Cy combined per atom of metal.
Gold—as $\text{HAuCl}_4\text{Aq}$ .....	0.18	9.14	39.4	2.1	37.3	4.08
as $\text{HAuCl}_4\text{Aq}$ .....	0.025	1.24	24.9	20.0	4.9	3.99
as $\text{HAuCl}_4\text{Aq}$ .....	0.02	1.01	19.8	15.9	3.9	3.86
as $\text{HAuCl}_4\text{Aq}$ .....	0.04	2.03	19.8	11.8	8.0	3.94
as $\text{HAuCl}_4\text{Aq}$ .....	0.07	3.55	19.8	5.75	14.05	3.98
as $\text{HAuCl}_4$ large excess NaOH .....	0.02	1.01	19.8	18.1	1.7	1.7
as metal "leaf".....	0.030	1.523	39.0	35.9	3.1	2.03
" " .....	0.05826	2.99	19.8	13.05	6.75	2.28
" " .....	0.07715	3.916	19.8	10.25	9.65	2.44
Mercury—as $\text{HgCl}_2\text{Aq}$ .....	0.1	5.0	19.8	9.1	10.7	2.14
as $\text{Hg}(\text{NO}_3)_2\text{Aq}$ .....	0.05	2.5	19.8	14.45	5.35	2.14
as $\text{Hg}(\text{NO}_3)_2\text{Aq}$ .....	0.1	5.0	19.8	9.2	10.6	2.12
as $\text{HgCl}_2\text{Aq}$ .....	0.4	20.0	50.0	6.95	43.05	2.15
as $\text{HgCl}_2\text{Aq}$ + excess NaOH.....	0.4	20.0	50.0	7.3	42.7	2.13
Nickel—as $\text{NiSO}_4\text{Aq}$ .....	0.0396	6.77	39.6	15.7	23.9	3.53
as $\text{NiSO}_4\text{Aq}$ .....	0.0396	6.77	39.6	15.45	24.05	3.55
as $\text{NiSO}_4\text{Aq}$ .....	0.0198	3.78	19.8	7.85	11.95	3.53
as $\text{NiSO}_4$ + excess NaOH	0.0198	3.78	19.8	7.85	11.95	3.53
Cobalt—as $\text{CoCl}_2\text{Aq}$ .....	0.105	17.86	99.0	14.4	84.6	4.73
as $\text{CoCl}_2\text{Aq}$ , titrated after one hour.....	0.0315	5.36	40.0	14.0	26.0	4.85
as $\text{CoCl}_2\text{Aq}$ , titrated im- mediately .....	0.0315	5.36	40.0	15.3	24.7	4.61
as $\text{CoCl}_2\text{Aq}$ , titrated im- mediately .....	0.042	7.15	40.0	7.4	32.6	4.56
as $\text{CoCl}_2\text{Aq}$ + 0.5 gram NaOH, titrated im- mediately .....	0.042	7.15	40.0	7.6	32.4	4.52
as $\text{CoCl}_2\text{Aq}$ + 0.32 gram NaOH, titrated after five hours.....	0.042	7.15	50.0	16.6	33.4	4.67
as $\text{CoCl}_2\text{Aq}$ + 0.16 gram NaOH, titrated after five hours.....	0.042	7.15	50.0	16.7	33.3	4.66
as $\text{CoCl}_2\text{Aq}$ + ten cc. ammonia, titrated after five hours ....	0.042	7.15	50.0	16.75	33.25	4.65

Metal.	Gram metal added.	Atoms metal added.	Equivalents KCy taken.	Equivalents Cy found by titration.	Difference(=equiv- alents of Cy com- bined).	Equivalents Cy combined per atom of metal.
Cobalt—as $\text{CoCl}_2$ Aq alone, titrated after five hours..	0.042	7.15	50.0	16.5	33.5	4.68
Platinum—as $\text{H}_2\text{PtCl}_6$ .....	0.06	3.1	19.8	19.4	0.4	0.13
as $\text{H}_2\text{PtCl}_6$ .....	0.125	6.4	39.4	38.6	0.8	0.125
as $\text{H}_2\text{PtCl}_6$ + excess NaOH.....	0.12	6.2	19.8	19.2	0.6	0.10
Silver—as nitrate (standard)..	....	...	...	...	...	2.0
as AgCl.....	0.06475	6.0	20.1	8.1	12.0	2.0
as AgCl.....	0.06475	6.0	20.1	8.05	11.95	1.992
as AgI.....	0.06475	6.0	20.1	8.15	12.05	2.008
as AgI.....	0.06475	6.0	20.1	8.1	12.0	2.0
as AgBr.....	0.05385	5.0	20.1	10.1	10.0	2.0
as $\text{Ag}_2\text{S}$ dissolved in $\text{HNO}_3$ .....	0.05385	5.0	20.1	10.2	9.9	1.98
Manganese—as $\text{MnCl}_2 + \text{NH}_4\text{Cl}$	0.0242	4.39	19.9	17.0	2.9	0.66
as $\text{MnCl}_2 + \text{NH}_4\text{Cl}$	0.0122	2.2	19.9	18.25	1.65	0.75
as $\text{MnCl}_2 + \text{NH}_4\text{Cl}$	0.0122	2.2	19.9	18.7	1.2	0.55
Copper—series 10 .....	....	..	...	...	about	3.43
—with excess ammonia. ....	....	..	...	..	approaches	3.0
Zinc—series 9 .....	....	..	...	...	under	4.0
—with excess NaOH.....	....	..	...	..	approaches	0.0
Cadmium—series 11, varies .....	....	..	...	...	...	0.5
—with excess ammonia ....	....	..	...	..	approaches	0.0

Upon standing the final precipitates of silver iodide increased greatly in presence of cobalt, manganese, platinum, and auric compounds : with zinc and copper the tendency was in the reverse direction.

SERIES 13.—EFFECTS OF OXIDIZING AGENTS.

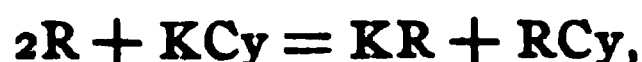
Set I.—These oxidizing solutions were standardized immediately before use by standard thiosulphate, or permanganate, or by both methods. Measured volumes were then added to ten cc. lots of fifth-normal potassium cyanide solution, which were then titrated with twentieth-normal silver nitrate, using three to five cc. ammonia and one-tenth gram potassium iodide as indicator.

Oxidising agent.	Gram added.	Atoms added.	Equivalents of KCy taken.	Equivalents of Cy found by titration.	Difference (=equiv- alents of Cy oxid- ized).	Equivalents of Cy oxidized by one atom.
Iodine (dissolved in KI).	0.051	4.0	19.8	18.0	1.8	0.448
" " " "	0.102	8.0	19.8	15.95	3.85	0.479
" " " "	0.204	16.0	19.8	12.05	7.75	0.482
" " " "	0.306	24.0	19.8	7.95	11.85	0.49
" " " "	0.255	20.0	9.95	0.3	9.65	0.481
" " in KOH	0.356	27.2	20.0	9.1	10.9	0.40
Bromine (water solution)	0.039	4.9	19.8	17.5	2.3	0.47
" " " "	0.196	24.5	19.8	7.75	12.05	0.493
" " " + KOH .....	0.196	24.5	19.8	8.4	11.4	0.465
Chlorine (water solution)	0.0275	7.8	19.8	16.05	3.75	0.481
" " " "	0.055	15.6	19.8	12.2	7.6	0.488
Chlorine (active chlorine in bleaching powder).	0.0542	15.3	19.8	12.4	7.4	0.483
Chlorine (active chlorine in bleaching powder).	0.1085	30.6	19.8	4.95	14.85	0.484
Oxygen (available oxygen in twenty cc. hydrogen peroxide).....	....	6.5	19.8	19.7	0.1	0.015
Oxygen (available oxygen in seventy-five cc. hy- drogen peroxide).....	....	24.3	19.8	19.4	0.3	0.012
Oxygen (available oxygen in 0.11 gram sodium peroxide).....	....	4.7	19.8	19.8	0.0	0.0
Oxygen (available oxygen in 0.38 gram sodium peroxide left two hours) .....	....	15.7	19.8	19.7	0.1	0.06
Oxygen (available oxygen in fifty cc. saturated solution of barium peroxide) .....	....	1.55	19.8	19.8	0.0	0.0
Oxygen (available oxygen in 100 cc saturated so- lution of barium per- oxide) .....	....	3.1	19.8 {	19.8 to 19.85	0.0 to 0.05	0.0 to 0.016

In the case of iodine, bromine, and chlorine (whether free or in bleaching powder), the proportion of cyanide oxidized evi-



dently approaches that corresponding to the well known equation :



and more closely as the proportion of halogen to cyanogen increases. The variation from five-tenths in the values in the last column may be due to the action of the ammonia added as indicator. The active chlorine in the bleaching powder was determined from the iodine it liberated from potassium iodide in presence of free hydrochloric acid ; in neutral solutions it only liberated about one-twelfth as much iodine ; but its effect on cyanide in alkaline solution corresponds to the full value of the chlorine set free by acid.

The slight effect of potassium nitrate, and of dichromate, on long standing (see series 8), may be due to oxidation ; potassium chlorate was without observable effect.

### *Permanganates.*

*Set II.*—A number of experiments were made with permanganates, to ascertain the extent to which they oxidized cyanide. The first effect of adding potassium permanganate is to turn the cyanide solution blue, then green and brown, a precipitate (manganese dioxide) falling. The precipitated oxide made it difficult to observe the end of titration ; this was remedied to some extent by adding ammonium chloride. The results varied irregularly with time.

The following tests were made with ten cc. tenth-normal potassium cyanide solution, cyanogen being determined after addition of small amounts of 0.0925 normal potassium permanganate solution.

	(a)	(b)	(c)	(d)
Potassium permanganate added—cc.....	0.0	4.0	4.0	10.0
“ “ “ gram....	0.0	0.01168	0.01168	0.0292
“ “ “ molecule	0.0	0.74	0.74	1.85
Atoms oxygen liberated if reduced to MnO	0.0	1.85	1.85	4.63
“ “ “ “ “ to MnO <sub>2</sub>	0.0	1.11	1.11	2.77
Time of contact before titration—minutes .	...	15.0	30.0	30.0
Equivalents cyanogen found by titration..	19.8	18.9	18.55	15.8
Difference from (a) = equivalents Cy oxidized.....	0.0	0.9	1.35	4.0

With larger additions of permanganate it was impossible to observe the end-reaction.

From the results shown in series 12 and 13 it is evident that there is a close approximation to constancy in the number of equivalents of cyanogen combined or oxidized by each atom or molecule of some of the interferents. Evidently also, if the conditions can be so adjusted as to secure absolute constancy in the amount of cyanide combined or decomposed by a unit of interferent, a method is obtained for the volumetric estimation of this interferent by titrating with silver nitrate two equal quantities of potassium cyanide, to one of which the interferent has been added. Such is the basis of Denigès' method of estimating silver. The improved method for nickel, published by Thomas Moore,<sup>1</sup> is an application of the same principle.

#### SERIES 14.—EFFECT OF THIOSULPHATES.

Previous experiments had shown, as had been expected, that the addition of a thiosulphate increased the amount of silver nitrate required in a given estimation. In the following series of tests potassium cyanide solution was treated with various quantities of sodium thiosulphate, and then cyanogen was estimated by tenth-normal silver nitrate, using five cc. ammonia and one-tenth gram potassium iodide as indicator.

The sodium thiosulphate solution used in I and II contained 0.0415 gram of the crystals per cubic centimeter (1 cc. = 1.66 molecules sodium thiosulphate), that used in III and IV 0.01 gram per cc. (1 cc. = 0.4 molecule).

*Set I.*—Twenty-five cc. fifth-normal potassium cyanide solution titrated with tenth-normal silver nitrate solution.

Sodium thiosulphate added.		Equivalents of cyanogen indicated by titration.	Difference from amount present.	Excess cyanogen for one molecule sodium thiosulphate.	No. of molecules sodium thiosulphate equal in effect to one equivalent cyanogen.
Grams.	Molecules.				
0.0	0.0	49.6	0.0	....	....
0.207	8.3	50.8	1.20	0.145	6.91
0.415	16.6	52.12	2.5	0.15	6.64
0.83	33.3	54.4	4.8	0.144	6.91
1.04	41.6	55.8	6.2	0.149	6.71
1.275	50.0	56.8	7.2	0.144	6.95
1.48	58.3	57.6	8.0	0.137	7.30

<sup>1</sup> *Chem. News*, 72, 93.

*Set II.*—Twenty cc. fifth-normal potassium cyanide solution titrated with tenth-normal silver nitrate solution.

Sodium thiosulphate added.					
Grams.	Molecules.	Equivalents of cy- anogen indicated by titration.	Difference from amount present.	Excess cyanogen for one molecule sodium thiosul- phate.	No. of molecules sodium thiosul- phate equal in ef- fect to one equiva- lent cyanogen.
0.0	0.0	39.6	0.0	....	....
0.415	16.6	41.6	2.0	0.12	8.3
0.830	33.3	43.8	4.2	0.126	7.95
1.245	50.0	46.2	6.6	0.132	7.12
1.660	66.6	48.6	9.0	0.135	7.4
2.075	83.3	51.0	11.4	0.137	7.3

*Set III.*—Ten cc. fifth-normal potassium cyanide solution ti-  
trated with twentieth-normal silver nitrate solution.

0.0	0.5	20.1	0.0	....	....
0.125	5.0	20.55	0.45	0.09	11.1
0.25	10.0	20.95	0.85	0.085	11.7
0.375	15.0	21.4	1.30	0.087	11.55
0.5	20.0	21.8	1.70	0.085	11.76
0.75	30.0	22.6	2.50	0.083	12.0
1.0	40.0	23.5	3.45	0.086	11.9

*Set IV.*—Five cc. fifth-normal potassium cyanide solution  
titrated with twentieth-normal silver nitrate solution.

0.0	0.0	10.05	0.0	....	....
0.125	5.0	10.55	0.5	0.1	10.0
0.25	10.0	10.85	0.8	0.08	12.0
0.375	15.0	11.15	1.1	0.073	13.0
0.5	20.0	11.45	1.4	0.07	14.0
0.75	30.0	12.1	2.05	0.068	15.0
1.0	40.0	13.05	3.0	0.075	13.3

*Set V.*—In these tests small amounts of potassium cyanide  
were treated with larger proportions of thiosulphate, and titra-  
ted with twentieth-normal silver nitrate, using as indicator one-  
tenth gram potassium iodide and five cc. ammonia.

	(a.)	(b.)	(c.)	(d.)	(e.)
Sodium thiosulphate added, grains...	0.1	0.415	0.5	1.25	1.25
“ “ “ molecules	4.0	16.6	20.0	50.0	50.0
Equivalents of KCy taken.....	0.0	0.0	2.0	2.0	20.0
Equivalents of cyanogen indicated by titration .....	0.1	0.6	2.8	3.3	22.75

	(a.)	(b.)	(c.)	(d.)	(e.)
Difference = excess of cyanogen indicated .....	0.1	0.6	0.8	1.3	2.75
No. of equivalents cyanogen equal in effect to one molecule $\text{Na}_2\text{S}_2\text{O}_3$ .....	0.025	0.036	0.04	0.026	0.055
Number of molecules $\text{Na}_2\text{S}_2\text{O}_3$ equal in effect to one equivalent cyanogen ..	40.0	27.0	25.0	38.5	18.1

*Set VI.*—Varying the indicator—potassium iodide—in presence of thiosulphate, using in each case five cc. fifth-normal potassium cyanide solution and three cc. ammonia ; volume fifty cc.

	(a.)	(b.)	(c.)	(d.)
Sodium thiosulphate added, grams ....	0	0.25	0.25	0.25
" " " molecules	0	10.0	10.0	10.0
Potassium iodide used, grams .....	0.1	0.1	0.5	1.0
Equivalents cyanogen indicated by titration .....	10.05	11.45	11.0	10.75
Error in cyanogen indicated .....	....	1.4	0.95	0.7

The end reaction is rendered somewhat indistinct by thiosulphates, and an appreciable error is introduced by 0.01 gram of sodium thiosulphate. For a given amount the actual error in estimating cyanogen increases, the percentage error decreases, with the proportion of cyanide.

The error is far less with the iodide indicator than without it (see series 6, VIII) ; a large increase in the amount of iodide added decreases the error somewhat further. When the proportion of thiosulphate is small, titration gives an excess of about one equivalent of cyanogen for seven molecules sodium thiosulphate (or one milligram for sixty milligrams crystallized sodium thiosulphate). With relatively large amounts of thiosulphate the error introduced per molecule is less, with a large excess about one equivalent cyanogen for thirty-five or forty of thiosulphate.

No satisfactory remedy was found ; various oxidizing agents were tried.

#### SERIES 15.—EFFECT OF SULPHIDES.

Hydrogen sulphide (a saturated water solution) and alkaline sulphides, were added to potassium cyanide in various proportions : on titrating with silver nitrate by the method of Denigès the dark precipitate of silver sulphide invariably appeared before the end was reached, gradually redissolving at first, but be-

coming permanent before the silver added corresponded to the whole of the cyanogen present, except when the amounts of sulphide were trifling. The device recommended by MacArthur and by Denigès, of precipitating by an alkaline plumbite or its equivalent, was tested and found to work well, except with large proportions of sulphide when slight errors are introduced. It is advisable to use as slight an excess of lead as possible (see effect of lead plumbite, in series 8). It appears to make no difference whether the lead be added as plumbite, or as nitrate following an excess of caustic alkali, provided a sufficient excess of alkali be added. The filtering off of the precipitated lead sulphide is an inconvenience: attempts were made to titrate directly, without filtering off this precipitate, which settles rapidly and affords a good background for observing the end-reaction.

#### TITRATION IN PRESENCE OF SULPHIDES.

##### *Adding Sodium Plumbite without Filtering off the Lead Sulphide.*

*Set I.*—Using in each case twenty cc. fifth-normal potassium cyanide, titrating with tenth-normal silver nitrate, after addition of five cc. ammonia and one-tenth gram potassium iodide.

Saturated fiftieth-normal hydrogen sulphide

water added, cc .....	0	0	10.0	10.0
Lead added (as sodium plumbite + excess NaOH) grams .....	0	0.05	0.05	0.05
Tenth-normal silver nitrate solution required, cc.....	19.8	19.7	20.7	20.8
Equivalents of cyanogen indicated.....	39.6	39.4	41.4	41.6

Under these conditions high results were always obtained. Moreover, in presence of the precipitated lead sulphide, the cloud of precipitated silver iodide cleared in about a minute, reappearing on increasing the silver nitrate to 21.7 cc., again clearing and reappearing permanently with 22.1 cc. Hence the apparent amount of cyanogen, found by titrating to a permanent precipitate without filtering off lead sulphide, might be 44.2 equivalents instead of an actual 39.6, an excess of over ten per cent.

##### *Adding Sodium Plumbite and Filtering off the Precipitate Formed.*

*Set II.*—Twenty cc. of fifth-normal potassium cyanide solution were treated with six cc. of hydrogen sulphide water: sodium

plumbite was added, the whole was transferred to a cylinder, shaken well, allowed to settle; twenty cc. of the clear liquid were removed by a pipette and treated as in the previous case.

cc. tenth-normal silver nitrate required: 7.90 (for two-fifths of the whole).

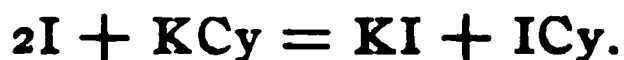
Equivalents of cyanogen indicated:  $7.9 \times 2 \times \frac{5}{2} = 39.5$ , instead of 39.7.

A similar test at another time gave 44.0 equivalents cyanogen instead of 44.6.

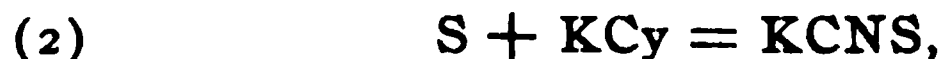
Attempts were made to retain the sulphur in solution as a thio-salt, by the addition of alkaline arsenites, stannates, and antimonites; these all failed, the liquid becoming dark-colored as the amount of uncombined potassium cyanide decreased with the progress of titration; though the actual precipitation of silver sulphide seemed to be preventable. The added salts were themselves found to interfere somewhat.

Various oxidizing agents were experimented with, but all that affected alkaline sulphides appeared to decompose potassium cyanide itself, either directly, or by liberating sulphur, which slowly dissolved with formation of thiocyanate. The halogens readily oxidized sulphides; the peroxides of hydrogen and alkalis were slow and incomplete in action.

A promising method for the removal of sulphide was based on the fact that a weak solution of iodine precipitates sulphur from alkaline sulphides, this redissolving in a minute or two to form thiocyanate. As the direct decomposition of potassium cyanide by iodine under these conditions approximates to the reaction:



and with potassium sulphide and cyanide together:



so that two atoms of iodine in either case decompose one molecule of cyanide, it seemed probable that the interference of small quantities of sulphide could be corrected by adding a constant amount (a slight excess) of a weak iodine solution, and introducing a correction for the amount of added iodine, which correction should be independent of the amount of sulphide oxi-

dized. A number of preliminary experiments confirmed this, subsequent titration with silver nitrate giving, with the correction, quite accurate determinations of the cyanide taken, when the amount of sulphide was small and other reducing agents were absent; with larger proportions of sulphide an appreciable error was introduced, the extent and variation of which were not determined.

*Oxidation of the Sulphide by Iodine.*

*Set III.*—Small quantities of a freshly prepared solution of potassium sulphide (fiftieth-normal, so that 1 cc.=0.00032 gram sulphur) were added to portions of fifth-normal potassium cyanide solution, then a weak solution of iodine in potassium iodide solution (1 cc. = 0.0015 gram iodine) was added to oxidize the sulphide, and cyanogen was estimated as usual.

TO ASCERTAIN THE CORRECTION FOR IODINE ADDED.

	(a)	(b)	(c)	(d)
cc. fifth-normal potassium cyanide taken...	5.0	5.0	10.0	10.0
cc. iodine solution added.....	0.0	30.0	0.0	15.0
cc. twentieth-normal silver nitrate required.	10.05	8.15	20.15	19.2
Correction to be added for iodine.....	....	1.9	....	0.95
		for 30 cc.		for 15 cc.

USE OF CORRECTION IN PRESENCE OF SULPHIDES.

	(e)	(f)	(g)	(h)	(i)	(j)	(m)
cc. fifth-normal potassium cyanide solution taken	10.0	10.0	10.0	10.0	10.0	5.0	5.0
cc. fiftieth-normal potassium sulphide solution added .....	0.5	1.0	2.0	2.0	5.0	0.5	5.0
Milligrams sulphur added as potassium sulphide	0.15	0.32	0.64	0.64	1.6	0.16	1.6
cc. iodine solution used..	15.0	15.0	15.0	15.0	15.0	30.0	30.0
cc. twentieth-normal silver nitrate required to precipitate .....	19.2	19.2	19.2	19.15	...	8.15	8.35
Correction for iodine.....	0.95	0.95	0.95	0.95	...	1.9	1.9
Equivalents of cyanogen found .....	20.15	20.15	20.15	20.10	...	10.05	10.25
Error .....	0.0	0.0	0.0	−0.05	...	0.0	+0.2

In (h) the iodine added was insufficient to oxidize all the sulphide, in (m) an appreciable amount of sulphur separated and did not redissolve, thus introducing an essential error, and also slightly obscuring the end-reaction; this was observed in other

experiments with larger proportions of sulphides; in other experiments with smaller amounts than above no error was observed.

There seems to be no objection to the use of iodine for removing small quantities of sulphide, provided other reducing agents are absent. This avoids the filtration necessitated by the use of alkaline plumbites; when larger proportions of sulphides make it advisable to use lead, it should be added in very slight excess, and a fairly large excess of alkali should be added with it.

#### ESTIMATION OF CYANOGEN IN ALKALINE CYANIDES: PROCEDURE.

To the solution, in which cyanogen is to be determined, add five cc. commercial ammonia water and two cc. of a five per cent. solution of potassium iodide; titrate in the cold with dilute standard silver nitrate till a faint permanent cloud forms. This is best seen by using a thin flask with a dark back-ground.

This quantity of ammonia is suitable for titrating 25 to 100 cc. of solution; for rapid approximate work, where ten cc. of sample is usually taken, one cc. each of ammonia and iodide solution will be sufficient.

The two indicators may be conveniently combined in one solution. If sufficient ammonia is already present, no more should be added; if a great deal is present a larger addition of iodide (say one gram) will reduce error. Thiosulphates will cause some error, also partially remedied by addition of more iodide.

In presence of *sulphides* in small amount, replace the potassium iodide by five or ten cc. of a solution of about one-half gram iodine and two or three grams potassium iodide in 100 cc. of water, allow to stand five minutes, then add ammonia and titrate. To the result add a correction, which is the difference between parallel tests (i) on some pure dilute potassium cyanide solution, (ii) on an equal amount of potassium cyanide *plus* five or ten cc. of iodine solution.

If the amount of sulphide is large, or if other reducing agents are also present, take twice the usual volume of solution, add some soda, then sodium plumbite in very slight excess, shake well, make up to a definite volume, filter, and use one-half the clear filtrate for titration, rejecting the first few cubic centimeters filtered.



In presence of zinc add a considerable excess of sodium or potassium hydroxide and proceed as above; test the end precipitate with more alkali (if it dissolves add more alkali and continue titration); if insoluble, the cyanogen found represents that contained in potassium zinc cyanide as well as in free potassium cyanide.

The free potassium cyanide can be accurately determined by acidulating another portion of the solution with hydrochloric acid, evaporating till all hydrocyanic acid is expelled, estimating zinc by standard ferrocyanide, and subtracting four equivalents cyanogen or potassium cyanide for each atom of zinc found (or for one milligram zinc subtract one and six-tenths milligram cyanogen or four milligrams potassium cyanide. The free potassium cyanide may be more rapidly and roughly determined by adding first a few drops of a five per cent. solution of potassium ferrocyanide, and titrating directly with silver nitrate until a faint flocculent precipitate forms (using  $a$  cc.); then to the same portion adding ammonia, potassium iodide, and soda, and titrating *total cyanogen* (using  $b$  cc. altogether). The value  $a$  minus a correction indicates cyanogen in free or "available" potassium cyanide: and  $(b - a)$  plus the same correction indicates that in double zinc cyanide, the error and correction is increased if free caustic alkali were originally present, and varies slightly with the time occupied in titrating. According to Bettel  $a - 0.086 (b - a)$  represents the cyanogen "available," and  $(b - a) \div 0.921$  gives that in the double cyanide, *if free alkali were originally absent*.

In presence of small amounts of copper the cyanogen combined as double copper cyanide is very approximately calculated by allowing three to four equivalents cyanogen for one atom of copper; the copper being readily estimated colorimetrically by ammonia after expelling hydrocyanic acid with nitric or sulphuric acid.

In presence of calcium, magnesium, or manganese, add ammonium chloride; in presence of aluminum or lead add caustic alkali.

The quantities of gold, silver, and other interfering substances in working solutions are almost always too small to affect the results appreciably; if present in larger proportions, or if bromine or other oxidizers have been added, the amounts of cy-

anogen held by them can be determined approximately from the data in series 12 and 13.

Generally, with impure solutions, the results of titration by this method are more accurate than those obtained by the ordinary Liebig method; with pure solutions the results are practically identical, and in nearly all cases the end-reaction is sharper and an estimation can be more rapidly carried out.

108 grams silver, or 170 grams silver nitrate correspond to 52 grams cyanogen or 130 grams potassium cyanide.

The standard silver solution used may be, with advantage, quite dilute; preferably not over twentieth normal, or one-half per cent. silver.

For technical purposes it is common to take 1.305 grams silver nitrate crystals per 100 cc. of water, when each cc. corresponds to one centigram of potassium cyanide (or four milligrams of cyanogen); or, taking samples of ten cc. each, one cc. of standard silver solution used represents one-tenth of one per cent. potassium cyanide in the liquid tested.

If prepared by dissolving the weighed metal it is not generally necessary to expel all acid. Satisfactory results have also been obtained by using a standard ammoniacal silver solution, made by dissolving pure silver in commercial nitric acid, and adding a slight excess of ammonia.

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## QUALITATIVE SEPARATIONS WITH SODIUM NITRITE IN ABSENCE OF PHOSPHATES, ETC.<sup>1</sup>

BY GILLETTE WYNKOOP.

Received March 8, 1897.

IF a solution of sodium nitrite be added to a solution of ferrous sulphate, the ferrous sulphate solution at first turns a deep brown, and in a short time a greenish brown flocculent precipitate forms, which gradually changes to a fine yellow precipitate, and at the same time a copious evolution of nitrous fumes takes place. If there is a small amount of free acid present in the ferrous sulphate solution, the yellow precipitate occurs almost immediately, and more rapidly still if heated.

A. Peccini and M. Zuco<sup>2</sup> obtained a precipitate similar to this, but used barium nitrite instead of sodium nitrite. Barium

<sup>1</sup> Read at the meeting of the New York Section, March 5, 1897.

<sup>2</sup> *J. Chem. Soc.*, 50, 448.

sulphate was the first precipitated, and the liquid turned brown. Finally an ochre-colored powder separated accompanied by an evolution of nitric oxide. From a quantitative determination of the nitric oxide evolved, the authors considered the precipitate to be a basic ferric nitrate. However, in my investigation, no test has been found for the nitric acid in the precipitate when precipitated with sodium nitrite.

If a ferric salt be used instead of a ferrous, as ferric chloride, the solution at first turns deep red, and evolution of nitrous fumes occurs almost immediately, with the formation of a dark brown precipitate. As with the ferrous sulphate, a small amount of free acid and heat aids the precipitation. If treated in this way the iron will be completely precipitated in a few minutes, and when the heat is withdrawn, the precipitate quickly settles to the bottom of the containing vessel, leaving the solution perfectly clear above.

This precipitate was investigated by L. Pesci,<sup>1</sup> who considered it to be the dimeta ferric hydroxide.  $\text{Fe}_2\text{O}_3(\text{OH})_2$ . In precipitating it he excluded air, and obtained a brown precipitate, soluble in water, from which solution it was again reprecipitated by strong nitric acid, but dissolved in excess of acid. In precipitating it without excluding the air, the precipitate was apparently as insoluble in water as that produced with ammonium or sodium hydroxide.

Observing the above reactions, I thought it would be of interest to see what effect sodium nitrite had upon salts of other metals of the iron and chromium group, and have obtained the following results: Of the common elements of the iron and chromium groups, iron, aluminum and chromium are completely precipitated by sodium nitrite, if the solution is boiled for a short time, while cobalt nickel, zinc and manganese are unaffected, if a small amount of free acid is present in the solution of the salts. At first neutral solutions were used, in which case small amounts of cobalt, nickel, zinc and manganese were sometimes precipitated. But this never occurred when a few drops of hydrochloric acid were first added. In the cold, iron and some of the cobalt are precipitated (the cobalt being precipitated as the double nitrite of cobalt and sodium), while

<sup>1</sup> *J. Chem. Soc.*, 1888, 1252.

chromium and aluminium do not come down until heated nearly to the boiling-point.

It was my next endeavor to ascertain whether the iron and chromium precipitate carried down with it any zinc, as is the case when precipitated with sodium hydroxide or ammonia. Qualitative experiments were here used instead of quantitative, as perhaps should have been done, but the results justify me in believing that at least no more than inappreciable quantities of zinc are carried down by the iron and chromium.

Various proportions of iron and chromium were added in small amounts of zinc solution and precipitated, the zinc always showing plainly in the filtrate. Twenty parts of ferric and chromic chloride were mixed with one part of zinc nitrate and the solution so diluted that it contained one part of zinc nitrate iron, to 5000 of solution, and then precipitated with sodium nitrite; grams zinc was easily detected in the filtrate. Equal amounts of chromium and zinc salts were mixed together, about two each, and precipitated with sodium nitrite; the precipitate was washed until the washings gave no test for zinc, then dissolved in hydrochloric acid; diluted and reprecipitated with barium carbonate, and filtered, the barium removed from the filtrate and the filtrate evaporated to forty cc., when a test was made for zinc with negative results. Tests were also made with iron and manganese. Equal quantities of manganous sulphate and ferric chloride were added together, precipitated and washed, and the precipitate tested for manganese with the sodium carbonate bead with negative results, showing that the separation is more complete than with barium carbonate. After these preliminary experiments, various mixtures of the salts of the iron and chromium groups were analyzed and the results were found as accurate, and in the case of iron and manganese, more accurate than with barium carbonate, and much more expeditious.

In case iron is present it is better to precipitate the iron in the ferrous state, as it gives a precipitate that is less bulky and gelatinous than the ferric iron, and therefore can be washed more quickly.

In a later paper I hope to give favorable results with the use of alkali nitrites in qualitative separations in the presence of phosphates, etc., as well as in quantitative separations.

## NEW BOOKS.

**TRAITÉ DE CHIMIE ORGANIQUE D'APRÈS LES THEORIES MODERNES.** BY A. BEHAL. With a preface by M. CH. FRIEDEL. VOL. I, ALIPHATIC COMPOUNDS. xv + 963 pp. Paris: Octave Doin. Price, 15 francs.

The first portion of this book (190 pages), deals with the general theories and methods of organic chemistry; the remainder (770 pages) is devoted to a systematic description of the compounds. The preface chiefly consists of a criticism of recent articles by Ostwald on the atomic theory and energy. The system of nomenclature used is that adopted by the Geneva congress which, in a text-book, is a new and very admirable departure. The general properties and methods of preparation of each class of compounds are clearly and fully given, while each separate compound is treated briefly, only its more important points being mentioned. There is much to be said in favor of this plan, since a dictionary, such as "Beilstein," can be consulted for more details and for references to the original papers, while subjects like alcohol or acetic acid, can only be satisfactorily dealt with in a technological work. In the first part the section on stereochemistry is particularly well written, the space formulæ being deduced separately from a consideration of isomerism and rotatory power. It is a pity that space has been occupied by sections on atoms and molecules, the treatment of which is of such an elementary character that it should be absolutely useless to any student of organic chemistry, and if it is not, then practically all the remainder of the book will be. Parts of the sections on manipulation are scarcely on a par with the excellence of the work; as a whole no mention is made of the open tube for combustions, the bayonet tube and Liebig's potash bulbs only are figured; the V. Meyer vapor-density apparatus shown is of the old form, as is also the nitrogen apparatus in the Dumas method. Raoult's apparatus for cryoscopic molecular weight determinations is described in which the cooling is effected by the evaporation of carbon disulphide in a current of air, but no mention is made of Beckmann's arrangement, which is simpler in construction and gives results of sufficient accuracy for ordinary purposes. These omissions are somewhat surprising in view of the fact that an excellent illustrated account is given of the surface-tension method of determining molecular weights, showing that the

author is fully alive to recent work in some directions. The omission of an index from this volume will doubtless be rectified in the remaining one, which is shortly to appear. J. B. T.

NOTES FOR CHEMICAL STUDENTS. BY P. T. AUSTEN, Ph.D., F.C.S. Second Edition. vi + 111 pp. New York: John Wiley & Sons. Price, \$1.50.

"This is not intended to be a text-book of chemistry but to explain or supplement certain topics which experience has shown often give the student more or less trouble and which are not sufficiently considered in the text-books. No attempt has been made to include all the difficulties that may be encountered." In judging of the book it must be considered in how far it fulfils the above objects as set forth in the preface. The elementary theory of chemistry is treated at some length; the chapter on weight relations leading up to the law of combination in definite and multiple proportions is clearly written; the law is illustrated by a number of good examples, and its enunciation is clearly and felicitously expressed. The tables in the section on stoichiometrical calculations will also be found useful. Unfortunately, accuracy and clearness of expression have been too frequently sacrificed to brevity. In a text-book intended for general use this would call for emphatic comment, but it may be assumed that the author's students will see the experiments referred to, and will receive the required cautions and extended exposition of the subject; to them, therefore, the book will probably prove serviceable. On page 37, in the foot-note, oxygen appears to be printed for nitrogen. The terms specific gravity, volume-weight, and density, are used as synonyms; is it not better to limit the last to the weight of a gas in hydrogen units, and employ the first to indicate its weight in units of air? J. B. T.

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#### ERRATA.

Page 293, (April number) twenty-eighth line, read "large" instead of "larger."

Page 295, thirty-fourth line, after "Series B" read "Time Constant: Masses Varied" instead of "Time Varied: Masses Constant."

Page 301, thirty-first line, read "inclusive" instead of "exclusive."

# THE JOURNAL

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## AMERICAN CHEMICAL SOCIETY.

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[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF THE U. S.  
DEPARTMENT OF AGRICULTURE, No. 27.]

### ON THE EXPERIMENTAL DETERMINATION OF THE HYDROTHERMAL VALUE OF A BOMB CALO- RIMETER.

BY H. W. WILEY AND W. D. BIGELOW.

Received March 29, 1897.

**F**OUR methods of determining the water equivalent of a bomb calorimeter and its accessories may be employed.

In the first place, a definite weight of a body whose thermal value is established may be burned in the system in the usual way, and the increase of temperature of the ambient water, the weight of which is also known, be determined. The difficulty attending this method is, in the first place, that the heat of combustion of the body employed rests upon experimental data, which themselves may be misleading.

In the second place, without a tedious and accurate chemical examination the experimenter cannot be assured of the purity of his materials.

This method may be varied by the successive combustions of double or triple the weight of the same body, and thus a factor be secured from which the water value of the metal parts of the system can be accurately calculated.

The second method of operation is one which is employed by Berthelot and Vieille. It consists in measuring the heat disengaged in mixing exact weights of water and sulphuric acid. The operation is carried on first in an ordinary calorimeter without the bomb, and afterwards the mixture is made in the

interior of the bomb placed in position. The experiment being made upon absolute or relative weights permits of a comparison of the quantities of heat produced in the two conditions. This method of procedure, exact as it is in theory, is somewhat difficult in practice, because of the slowness with which the thermal equilibrium is established between two masses of liquid separated by a metallic wall.

The third method of estimating the hydrothermal value of the calorimeter system consists in calculating it directly from the specific heats of the various materials composing it.<sup>1</sup> This is by far the most convenient method of proceeding, and where the exact weights of the different constituents are known it leaves little to be desired. The specific heats of all the various metals composing the calorimetric system have been very carefully determined. It is only in the case of alloys of rather uncertain composition that errors may result. Most of the alloys, however, which are employed have a definite composition, or nearly so, and since the specific heats of metals are so low, the slight variations from the standard which may occur do not produce any appreciable errors. In all cases the hydrothermal value of the system should be calculated from the weights of its various components, and the manufacturers should always be asked to furnish the exact weights of each metal or alloy in the apparatus.

The fourth method of determining the hydrothermal value of the system is the direct experimental one of mixtures, the same in principle as the processes which have been used for the determination of the specific heats of various bodies. In the method which is to be described the steps will be set forth which are necessary in the determination of the hydrothermal value by the method of mixtures when the difference in temperature between the two bodies of water is not very pronounced. In all the methods of mixture which have heretofore been employed a relatively small volume of water at a relatively high temperature has been mixed with a large volume at ordinary temperature. In order to secure this mixture it has been customary to have the added water contained in a platinum capsule and placed as quickly as possible in the water in the calorimeter which has been kept at a definite temperature. After thorough mixing the in-

<sup>1</sup> Principles and Practice of Agricultural Analysis, 3, 573.



crease of temperature furnishes the basis of the calculations. In this case it is necessary to put the containing platinum capsule also in the mixture, and its hydrothermal value must be previously calculated by the usual factors. Thermometers which extend over large intervals of degrees are necessarily less exact and less easily read than those in which the scales mark only a few degrees. We therefore determined to attempt to ascertain the hydrothermal value of the calorimetric system by measuring the changes of temperature by means of the Beckmann thermometer employed for determining molecular weights. The scales of these thermometers usually extend over a little more than  $5^{\circ}$ , and are divided so as to read to hundredths, and, by means of a cathetometer, to thousandths of a degree. By using two of these thermometers it is possible to work with masses which have a difference in temperature of a little over  $10^{\circ}$ . Before the thermometers are used they must be calibrated against each other in order to be certain that they register exactly the same differences of temperature as marked upon the scales. This having been accomplished, the two thermometers are placed in water at room temperature, and when equilibrium has been perfectly established the two scales are read. The thermometers are set in such a way that when this comparison is made the column of mercury in one shall be near the top of the scale, and in the other one near the zero point. The difference in readings in the two thermometers is thus directly established, and this having been done, the two can be used as a single thermometer.

Following are the analytical data obtained in ascertaining by direct mixture the hydrothermal value of a bomb calorimeter made for this division by O. S. Blakeslee, of Middletown, Conn.:

*Thermometers.*—The two thermometers employed were made by F. O. R. Goetze, of Jena glass. The dimensions of the thermometers are as follows: No. 1 (T<sub>1</sub>), distance from zero to bottom of bulb, twenty-five centimeters; length of scale, twenty-five centimeters; range of scale, zero to  $5.6^{\circ}$ . No. 2 (T<sub>2</sub>), distance from zero to bottom of bulb, 17.5 centimeters; length of scale, twenty-two centimeters; range of scale, zero to  $5.7^{\circ}$ .

Immersed in water, at a temperature of  $17.15^{\circ}$ , the readings of the two thermometers were as follows:

No. 1,  $0.030^{\circ}$ ; No. 2,  $4.540^{\circ}$ ; difference,  $4.510^{\circ}$ .

*Method of Using the Thermometers.*—In order to secure as wide a range of temperature as possible with the two thermometers set as above, No. 2 was used for fixing the initial temperature of the water in contact with the bomb, and No. 1 for fixing the initial temperature of the water added to the bomb system. By this method of use a difference in initial temperatures of approximately  $9^{\circ}$  was easily obtained.

*Method of Operation.*—It is useless to attempt to determine the hydrothermal value of the bomb system immersed in air alone. The excessive slowness with which changes of temperature take place between polished metal and air is sufficient to prevent any accurate results from being obtained in an experimental way. Even after standing for several hours in air, a piece of polished metal may have a temperature which differs from that of the ambient air by as much as one degree or more. It is therefore necessary, at the very commencement, to add to the bomb system a sufficient quantity of water to secure without any great delay a uniform temperature in all its parts. In the apparatus employed the vessel containing the bomb holds approximately 1700 cc. of water when the bomb is in place. It is important that the range of temperature on mixing be as great as possible, as very small differences in temperature make a marked difference in the computations. Theoretically to get the best results the water which is added to the bomb at a higher temperature should be equivalent in weight to the water surrounding the bomb before mixture plus the hydrothermal equivalent of the calorimeter. The temperature of the bomb system, therefore, on mixing will rise to the same degree that the temperature of the added water falls. If, however, this arrangement should be followed, the quantity of water in contact with the bomb would not be sufficient to secure promptly the equilibrium of temperature between the water and the metallic parts of the calorimeter. To avoid any confusion of ideas, it may be stated that in the following experiments the added water was always at the higher temperature and the bomb system at the lower. After a large number of trials it was found that the best results, in the case under consideration, were secured by adding about 1000 cc. of water to the bomb in order to fix its initial temperature, and about 700 cc. at a higher temperature at the time of the determination. It was found

that with 1000 cc. of water only a portion of the upper part of the bomb remained uncovered. Theoretically, the best adaptation of the system would be such that a sufficient quantity of water might be introduced to cover the whole of the bomb and the containing vessel still be large enough to hold the rest of the water added at the time of the determination. Practically, the small portion of the metal covering of the bomb which remained uncovered by the water in the experiments indicated below, by reason of its high conductivity, speedily acquired the temperature of the mixture.

*Manipulation.*—It is advisable to select a day for the experiments which is cloudy, and in which the changes in temperature are very slight. We were fortunate, after all the preliminary work necessary to the determination had been done, to secure such a day for the actual fixing of the hydrothermal value of the system. The changes in temperature during the day in which the experiments were made, *viz.*, March 9, 1897, were very slight, and in the room in which the experiments were carried on the whole change during the working day did not exceed 3°.

It is convenient to have the thermometer so set that the initial temperature of the bomb system is slightly below the temperature of the room. In this case the initial temperature of the added water is considerably above the room temperature, and hence the rate of cooling is a more important factor in this instance than in the other. The first point to be determined is the rate and direction of change of temperature of the water and the whole calorimetric system. The stirrer of the apparatus having been set in motion, the whole is allowed to stand for about half an hour. The reading of the thermometer immersed in the water is then commenced, and continued for about ten minutes, the thermometer being read at each minute during this time. These successive readings fix the rate of change of temperature. At the moment the readings cease the exact time is noted, in order that the whole amount of change before the mixing takes place may be computed. The next point to be determined is the rate of change of temperature in the water which is to be added. This is determined in exactly the same way, but, as a rule, five observations are sufficient to fix this point. At the moment of ceasing the readings, the time

is also noted. The rates of change having been thus fixed, the thermometer is removed from the calorimeter system, and a funnel, which has been immersed in the water to be added, and is therefore at exactly the same temperature, and which has been used as the stirrer for this water, is inserted in the place of the thermometer, and the water poured into the calorimeter. The beaker and appurtenances having been previously weighed, a reweighing of the empty beaker permits of the exact determination of the weight of the water added. A large balance, capable of carrying heavy weights on each arm, and yet reading accurately to 10 milligrams, is necessary in weighing these large bodies. In order to secure as even a temperature as possible for the added water, the following device is employed: The water is contained in a lip beaker. This beaker is set in a tin can, which is insulated on the outside by a non-conducting covering of felt or cotton. The beaker rests upon three corks in the bottom of the can, and is separated from the sides by four corks inserted in such a way as to hold it firmly in place. The insulating covering is pushed down at the top between the tin can and the beaker, so that the air enclosed in the interior space is prevented from circulation with the exterior air. By this device the added water, which in these experiments was always several degrees higher in temperature than the ambient air, was protected as much as possible from rapid cooling. The time which is consumed in pouring the water, replacing the thermometer, and adjusting other parts of the apparatus, is noted, and from these data the initial temperatures of the bomb system and of the added water are calculated for the moments in which the last of the water is added. The thermometer at first indicates a rapid rise of temperature, which is observed through a reading glass, until it reaches its maximum. As a rule, it will be found that the added water causes the thermometer to rise to a slightly higher point than is indicated by the final equilibrium of temperature due to the fact that the mixture of the water affects the mercury in the thermometer with a slightly greater ease than it secures an equilibrium in the metal system. The difference, however, between the maximum reading of the thermometer in any case, and the final equilibrium is never more than a few thousandths. The temperature of the mixture is now read

as before, at intervals of a minute, until two successive readings are practically identical. The readings are then continued for a few minutes until the temperature begins to fall, and the rate of fall is established. The correct temperature of the mixture is determined by taking the mean of the two readings which are nearest together after the slight fall from the maximum temperature, produced on the addition of the water, and correcting this reading as described below. From the data thus obtained the hydrothermal value of the system is calculated. As an illustration of the methods of calculation, the following data of four determinations made on the 9th of March, 1897, are given:

RECORD OF DETERMINATIONS, MARCH 9, 1897.

Weight of water in contact with the bomb, 997.1 grams.

Commencement of readings, 9 o'clock, 58 minutes.

Readings of thermometer ( $T_s$ ) at intervals of one minute,  $1.471^\circ$ ,  $1.468^\circ$ ,  $1.468^\circ$ ,  $1.468^\circ$ ,  $1.467^\circ$ ,  $1.465^\circ$ ,  $1.462^\circ$ ,  $1.460^\circ$ ,  $1.460^\circ$ ,  $1.460^\circ$ .

Ending of readings, 10 o'clock, 7 minutes.

Corrected temperature of water added,  $5.360^\circ$ , thermometer ( $T_1$ ).

Commencement of reading of water added, 10 o'clock, 8 minutes.

Readings at intervals of one minute,  $5.594^\circ$ ,  $5.560^\circ$ ,  $5.525^\circ$ ,  $5.485^\circ$ ,  $5.450^\circ$ ,  $5.420^\circ$ .

End of reading, 10 o'clock, 13 minutes.

Time of pouring, etc., 2 minutes.

Reading of thermometer after mixture ( $T_s$ ),  $4.285^\circ$ .

Other readings not entered.

*Calculation.*—The readings show that the temperature of the calorimetric system at the time of mixture was the same as that of the external air, so that no correction for changing temperature is to be applied. The temperatures of the added water show a change at the rate of  $0.030^\circ$  per minute. The time elapsed from the last reading until the pouring was complete was two minutes; hence the initial temperature of the added water was ( $T_1$ )  $5.360^\circ$ .

The weight of the added water was 710 grams. We then have the following data:

SUMMARY OF DATA.

Initial temperature of bomb and water ( $T_s$ ).....	$1.460^\circ$
Initial temperature of added water ( $T_1$ ) $5.360^\circ$ , ( $T_s$ )..	$9.870^\circ$
Weight of added water .....	710 grams
Final temperature of mixture ( $T_s$ ).....	$4.285^\circ$
Rise of temperature of calorimeter.....	$2.825^\circ$
Fall of temperature of added water .....	$5.585^\circ$

Then  $710 \times 5.585 = x \times 2.825$  in grams of water.

Whence  $x = 1403.7$ , and  $1403.7 - 997.1 = 406.6 =$  hydrothermal value of the calorimetric apparatus in grams of water.

The method of correcting the reading of the thermometer for the influence of the environment after mixture is given in the next determination.

#### SECOND DETERMINATION.

Weight of water in contact with the bomb, 1034.2 grams.

Commencement of reading, 10 o'clock, 45 minutes.

Readings of thermometer at intervals of one minute, ( $T_s$ ),  $0.608^\circ$ ,  $0.610^\circ$ ,  $0.613^\circ$ ,  $0.618^\circ$ ,  $0.620^\circ$ ,  $0.623^\circ$ ,  $0.626^\circ$ ,  $0.629^\circ$ ,  $0.632^\circ$ ,  $0.635^\circ$ ,  $0.638^\circ$ .

Ending of readings, 10 o'clock, 55 minutes.

First temperature of added water ( $T_1$ ),  $5.585^\circ$ .

Commencement of readings, 10 o'clock, 58 minutes.

Readings at intervals of one minute,  $5.550^\circ$ ,  $5.505^\circ$ ,  $5.465^\circ$ ,  $5.420^\circ$ ,  $5.375^\circ$  ( $T_1$ ).

End of readings, 11 o'clock, 3 minutes.

Time of pouring, 2 minutes.

The total time elapsed from the last reading of  $T_s$ ,  $0.638^\circ$ , in the calorimeter until the pouring was complete, was ten minutes. The temperature of the calorimeter system was increasing at the rate of  $0.003^\circ$  per minute. The total increase during this time was therefore  $0.030^\circ$ , and the initial temperature of the bomb and water at the moment the pouring was complete was therefore  $0.638^\circ + 0.030^\circ = 0.668^\circ$ . In the two minutes intervening between the completion of the pouring and the maximum reading of the thermometer, the change in temperature due to the environment is to be calculated from the observations of change after mixture; allowing for a temporary excess due to the time required for the metallic parts to assume the temperature of the ambient water. The rate of cooling, as determined by the final series of observations, was  $0.004^\circ$  per minute. The maximum temperature was observed at the end of two minutes, and the equilibrium of temperature was secured at the end of the third minute, when the observed temperature was ( $T_s$ )  $3.620^\circ$ . The loss of temperature for the three minutes which had elapsed since the completion of the mixture was therefore  $0.012^\circ$ , and this is to be added to the observed stable temperature ( $T_s$ )  $3.620^\circ$ . The final temperature of the mixture was therefore ( $T_s$ )  $3.620^\circ + 0.012^\circ = 3.632^\circ$ .

## SUMMARY OF DATA.

Reading of thermometer after mixture ( $T_s$ ),  $3.625^\circ$ .

Time, 2 minutes.

Readings at intervals of one minute ( $T_s$ ),  $3.620^\circ$ ,  $3.620^\circ$ ,  $3.618^\circ$ ,  $3.614^\circ$ ,  $3.610^\circ$ .

Initial temperature of bomb and water ( $T_s$ ) .....  $0.668^\circ$

Initial temperature of added water ( $T_l$ ),  $5.285^\circ$ ; ( $T_s$ ) .  $9.795^\circ$

Weight of added water..... 693.3 grams

Final temperature of mixture ( $T_s$ ).....  $3.632^\circ$

Rise of temperature of calorimeter.....  $2.964^\circ$

Fall of temperature of added water .....  $6.163^\circ$

Then  $6.163 \times 693.3 = x \times 2.964$ .

Whence  $x = 1441.6$ , and  $1441.6 - 1034.2 = 407.4 =$  hydrothermal value of apparatus in grams of water.

## THIRD DETERMINATION.

Weight of water in contact with the bomb, 1006.4 grams.

Commencement of reading, 11 o'clock, 50 minutes.

Readings of the thermometer ( $T_s$ ) at intervals of one minute,  $0.835^\circ$ ,  $0.840^\circ$ ,  $0.845^\circ$ ,  $0.850^\circ$ ,  $0.857^\circ$ ,  $0.865^\circ$ ,  $0.870^\circ$ ,  $0.875^\circ$ ,  $0.880^\circ$ ,  $0.885^\circ$ .

Ending of readings, 12 o'clock.

First temperature of added water ( $T_l$ ),  $5.585^\circ$ .

Readings of thermometer ( $T_l$ ) at intervals of one minute,  $5.555^\circ$ ,  $5.525^\circ$ ,  $5.490^\circ$ ,  $5.450^\circ$ ,  $5.415^\circ$ .

Ending of readings, 12 o'clock, 10 minutes.

Time of pouring, 2 minutes.

Reading of thermometer ( $T_s$ ) after mixture,  $3.914^\circ$  (maximum).

Time, 1 minute.

Readings of thermometer ( $T_s$ ) in mixture at intervals of one minute,  $3.912^\circ$ ,  $3.911^\circ$ ,  $3.910^\circ$ ,  $3.908^\circ$ ,  $3.903^\circ$ .

Interval from last reading of bomb until pouring was complete, 12 minutes.

Rate of change in temperature,  $0.005^\circ +$ .

Temperature of bomb, etc., at completion of pouring,  $0.0885^\circ + 60$ .

( $T_s$ ) =  $0.945^\circ$ .

Last reading of temperature of added water ( $T_l$ ),  $5.415^\circ$ .

Rate of change per minute,  $0.035^\circ -$ .

Time of pouring, 2 minutes.

Final temperature of added water at time pouring ceased ( $T_l$ ),  $5.415^\circ - 0.070^\circ = 5.345^\circ$ .

The rate of change in the temperature of the mixture was  $0.003^\circ$  per minute.

Time from end of pouring to concordant reading of the thermometer, 3 minutes.

Correction to be applied to concordant reading,  $3.911^\circ$  ( $T_s$ ),  $0.003 \times 3 = 0.009$ .

Corrected reading of temperature of mixture  $3.911^{\circ} + 0.009^{\circ} = 3.920^{\circ}$  (Ts).

#### SUMMARY OF DATA.

Initial temperature of bomb and water (Ts).....	0.945°
Initial temperature of added water (Tl), 5.345°; (Ts).	9.855°
Final temperature of mixture (Ts).....	3.920°
Weight of water added.....	704 grams.
Rise of temperature of calorimeter.....	2.975°
Fall of temperature of added water.....	5.935°

Then  $5.935 \times 704 = x \times 2.975$ .

Whence  $x = 1404.5$ , and  $1404.5 - 1006.4 = 398.1 =$  hydrothermal value of the calorimetric apparatus in grams of water.

#### FOURTH DETERMINATION.

Weight of water in contact with the bomb, 999.5 grams.  
 Commencement of readings, 2 o'clock, 8 minutes.  
 Reading of temperature of bomb (thermometer Ts) at intervals of one minute, 0.695°, 0.700°, 0.710°, 0.723°, 0.730°, 0.740°, 0.755°.  
 Ending of readings, 2 o'clock, 16 minutes.  
 First temperature of added water (Tl), 5.585°.  
 Commencement of readings, 2 o'clock, 17 minutes.  
 Readings of thermometer at intervals of one minute, 5.560°, 5.530°, 5.505°, 5.470°, 5.450°.  
 Ending of readings, 2 o'clock, 23 minutes.  
 Time of pouring, 2 minutes.  
 Reading of thermometer (Ts) after end of pouring, 3.870°.  
 Readings of thermometer (Ts) in mixture at intervals of one minute, 3.875°, 3.875°, 3.875°, 3.875°.

#### SUMMARY OF DATA.

Initial temperature of bomb and water (Ts).....	0.845°
Initial temperature of added water (Tl), 5.390°; (Ts).	9.900°
Final temperature of the mixture (Ts).....	3.875°
Weight of water added.....	709.0 grams
Rise of temperature of calorimeter.....	3.030°
Fall of temperature of added water .....	6.025°

Then  $709 \times 6.025 = x \times 3.03$ .

Whence  $x = 1409.8$ , and  $1409.8 - 999.5 = 410.3$  hydrothermal value of calorimetric apparatus in grams of water.

#### MEAN HYDROTHERMAL VALUE OF THE CALORIMETRIC SYSTEM.

From the data giving the hydrothermal values of the calorimeter, as determined in the foregoing experiments, we have the following table :



HYDROTHERMAL VALUE OF A BOMB CALORIMETER. 449

				Grams of water.
Hydrothermal value, first determination.....				406.6
“ “ second “ .....				407.4
“ “ third “ .....				398.1
“ “ fourth “ .....				410.3
				— —
Mean hydrothermal value .....				405.6

COMPARISON OF HYDROTHERMAL VALUE OBTAINED EXPERIMENTALLY WITH THAT SECURED BY CALCULATION.

The specific heats of the various parts of the calorimetric system, as computed from the standard specific heats of the materials composing them, are given in the following table :

Material.	Specific heat.
Brass.....	0.093
Steel .....	0.1097
Platinum.....	0.0324
Copper.....	0.09245
Lead .....	0.0315
Oxygen .....	0.2389
Glass.....	0.190
Mercury .....	0.0332
Hard rubber.....	0.33125
Tin ....	0.0548
Antimony .....	0.0523

HYDROTHERMAL VALUE OF THE BOMB CALORIMETER.

The hydrothermal value of the bomb calorimeter is calculated from the following data :

Material.	Weight. Grams.	Specific heat.	Hydrothermal value. Grams of water.
Platinum .....	160.00	$\times 0.0324$	$= 5.1840$
Steel .....	3,228.10	$\times 0.1097$	$= 354.1226$
Lead .....	46.00	$\times 0.0315$	$= 1.4490$
Brass .....	65.39	$\times 0.0930$	$= 6.0813$
Brittania metal {	tin.....	$687.69 \times 0.0548$	$= 37.6854$
	antimony ...	$53.49 \times 0.0523$	$= 2.7974$
	copper.....	$22.92 \times 0.09245$	$= 2.1192$
Mercury (estimated).....	21.76	$\times 0.0332$	$= 0.7224$
Glass (estimated).....	2.24	$\times 0.1900$	$= 0.4256$
Total hydrothermal value.....			410.5869

The two values, as obtained by direct determination and by calculation, are very near together. In the calculation above

given it should be borne in mind that it is difficult to determine the exact quantity of mercury in the thermometers without knowing the thickness of the sides of the bulb. It is also difficult to make the proper allowance for the glass part of the thermometer, inasmuch as it is not always immersed to exactly the same depth in the liquid, and further, the exact weight of the part immersed is not known, but can only be obtained approximately by calculation. Further, the tips of the wires, by which the firing of the bomb takes place, dip into the water, together with a portion of their caoutchouc covering. Further, the small piece of hard rubber by which one of the wires is insulated from the cover is not considered in the calculation. The hydrothermal value of these last-named bodies being slightly higher than metals, would have an appreciable influence upon the determination. The last thing to be mentioned in this connection is that while the specific heat of iron is pretty well established, it is known to vary slightly for the samples made in different localities and from different ores, and therefore the exact specific heat of steel, which composes the largest part of the calorimetric system, may be subject to slight variations. In view of this fact, it has been determined to use the mean of the two determinations as the correct expression for the hydrothermal value of the calorimeter in question, *viz.*,  $(405.6 + 410.6) \div 2 = 408.1$ .

#### CALCULATION BY THE FORMULA OF REGNAULT-PFAUNDLER.

The conditions of warming and cooling in the method of mixtures just described, are not precisely those which occur during the determination of the calorific power of a substance in the apparatus. The calculation of the influence of the ambient atmosphere upon the hydrothermal readings may, however, be conducted according to the formula of Regnault-Pfaundler.<sup>1</sup>

The calculation of the hydrothermal value in the case of the third determination given above, after correcting the end temperature according to the formula mentioned, is as follows:

Water value of the bomb, etc.,  $x$ .

Weight of water added to the bomb, 1006.4 grams.

Preliminary thermometric readings,  $t_1 = 0.835$ ,  $t_2 = 0.840$ ,  $t_3 = 0.845$ ,  $t_4 = 0.850$ ,  $t_5 = 0.857$ ,  $t_6 = 0.865$ ,  $t_7 = 0.870$ ,  $t_8 = 0.875$ ,  $t_9 = 0.880$ ,  $t_{10} = 0.885$ ,  $t_{n_1} = 0.945$ . ( $n_1 = 22$ ).

<sup>1</sup> Principles and Practice of Agricultural Analysis, 3, 572, 574.

Thermometric readings after pouring,  $\theta_1 = 0.945$ ,  $\theta_2 = 3.914$ ,  $\theta_3 = 3.912$ ,  $\theta_n = 3.911$ . ( $n = 4$ ).

Final thermometric readings,  $t'_1 = 3.911$ ,  $t'_2 = 3.910$ ,  $t'_3 = 3.908$ ,  $t'_n = 3.903$ .

From the formulas given above the following numerical values are computed :

$$v = \frac{t_{n_1} - t_1}{n_1 - 1} = 0.005.$$

$$v' = \frac{t'_{n_2} - t'_1}{n_2 - 1} = -0.003.$$

$$t = \frac{t_1 + t_2 + t_3 + \dots + t_n}{n_1} = 0.891.$$

$$t' = \frac{t'_1 + t'_2 + t'_3 + \dots + t'_{n_2}}{n_2} = 3.908.$$

$$\sum_{i=1}^{n-1} \theta_i = \theta_1 + \theta_2 + \theta_3 + \frac{\theta_n - \theta_1}{9} = 9.108.$$

Substituting these values in the Regnault-Pfaundler formula, the correction for the influence of the external air is

$$\Sigma \Delta t = \frac{0.005 - (-0.003)}{3.908 - 0.891} \left( 9.10 + \frac{3.911 + 0.945}{2} - (4 \times 0.891) \right)$$

$- (3 \times 0.005) = 0.006$ , which is added to the end temperature ( $\theta_n = 3.911$ ).

The computation is then made from the following data :

Corrected end temperature ( $\theta_n + 0.006$ ).....	3.917°
Beginning temperature ( $\theta_1$ ) .....	0.945°
Increase in temperature of bomb, etc.....	2.972°
Total calories .....	$x$ 2.972°
Weight of added water.....	704.0 grams
Temperature of added water.....	9.855°
Fall of temperature of added water.....	5.938°

Then  $5.938 \times 704 = x \times 2.972$ . Whence  $x = 1406.6$ , and  $1406.6 - 1006.4 = 400.2 =$  water value of calorimeter.

Calculated directly by the methods first given, the hydrothermal value in the third determination is found to be 398.1. After correcting for the end temperature by the Regnault-Pfaundler formula, and applying the calculation the hydrothermal value is found to be 400.2. It is thus seen that the two methods give almost the same results. For all practical purposes, therefore, it is not necessary to undertake the complicated computations required by the Regnault-Pfaundler formula, but the data may be calculated directly by the methods first given.

A RECALCULATION OF WEIN'S TABLE OF STARCH  
EQUIVALENT TO COPPER FOUND, BASED  
ON THE FACTOR 0.92.<sup>1</sup>

BY WILLIAM H. KRUG.  
Received March 24, 1897.

IN Wein's "Tabellen zur quantitativen Bestimmung der Zuckerarten" a table is given on page 41, by means of which the starch or dextrin can be directly obtained from the copper found by converting the starch into dextrose and determining the latter with Allihn's solution. This table is based on the factor 0.90, which assumes that the formula of starch is  $(C_6H_{10}O_5)_n$ , and that it is all converted into dextrose. Nägeli determined the formula of starch to be  $C_{48}H_{86}O_{41}$ , and if this be correct the factor becomes 0.918. Ost, working with the Sacchse method decided upon the factor 0.925. In view of all these conflicting data Wiley recommends the factor 0.92, a mean between the two last cited, which will give the analyst fairly accurate results. This factor has been used in the recalculation of the table.

Milligrams copper.	Milligrams starch or dextrin.	Milligrams copper.	Milligrams starch or dextrin.	Milligrams copper.	Milligrams starch or dextrin.	Milligrams copper.	Milligrams starch or dextrin.	Milligrams copper.	Milligrams starch or dextrin.
10..	5.6	30..	14.7	50..	23.8	70..	32.9	90..	42.2
11..	6.1	31..	15.2	51..	24.3	71..	33.4	91..	42.7
12..	6.5	32..	15.6	52..	24.7	72..	33.9	92..	43.1
13..	7.0	33..	16.1	53..	25.2	73..	34.3	93..	43.6
14..	7.5	34..	16.6	54..	25.7	74..	34.8	94..	44.1
15..	7.9	35..	17.0	55..	26.1	75..	35.1	95..	44.5
16..	8.3	36..	17.4	56..	26.5	76..	35.7	96..	45.0
17..	8.7	37..	17.8	57..	27.0	77..	36.2	97..	45.4
18..	9.2	38..	18.3	58..	27.4	78..	36.5	98..	45.9
19..	9.7	39..	18.8	59..	27.9	79..	37.1	99..	46.4
20..	10.1	40..	19.3	60..	28.3	80..	37.5	100..	46.8
21..	10.5	41..	19.7	61..	28.8	81..	38.0	101..	47.3
22..	11.0	42..	20.1	62..	29.3	82..	38.5	102..	47.7
23..	11.5	43..	20.6	63..	29.7	83..	38.9	103..	48.2
24..	12.0	44..	21.1	64..	30.2	84..	39.4	104..	48.7
25..	12.4	45..	21.5	65..	30.6	85..	39.9	105..	49.2
26..	12.9	46..	22.0	66..	31.1	86..	40.4	106..	49.7
27..	13.3	47..	22.4	67..	31.6	87..	40.8	107..	50.1
28..	13.8	48..	22.9	68..	32.0	88..	41.3	108..	50.6
29..	14.3	49..	23.4	69..	32.5	89..	41.8	109..	51.1

<sup>1</sup> Read at the meeting of the Washington Section, March 11, 1897.

Milligrams copper.	Milligrams starch or dextrin.	Milligrams copper.	Milligrams starch or dextrin.	Milligrams copper.	Milligrams starch or dextrin.	Milligrams copper.	Milligrams starch or dextrin.	Milligrams copper.	Milligrams starch or dextrin.
110..	51.5	152..	71.3	194..	91.5	236..	112.0	278..	132.8
111..	52.0	153..	71.8	195..	92.0	237..	112.5	279..	133.4
112..	52.4	154..	72.3	196..	92.5	238..	113.0	280..	133.9
113..	52.9	155..	72.8	197..	92.9	239..	113.5	281..	134.4
114..	53.4	156..	73.2	198..	93.4	240..	114.0	282..	134.9
115..	53.9	157..	73.7	199..	93.8	241..	114.5	283..	135.4
116..	54.3	158..	74.2	200..	94.4	242..	115.0	284..	135.9
117..	54.7	159..	74.7	201..	94.9	243..	115.5	285..	136.4
118..	55.3	160..	75.2	202..	95.4	244..	115.9	286..	136.9
119..	55.8	161..	75.6	203..	95.9	245..	116.5	287..	137.4
120..	56.2	162..	76.1	204..	96.3	246..	116.9	288..	137.8
121..	56.7	163..	76.6	205..	96.9	247..	117.4	289..	138.5
122..	57.1	164..	77.1	206..	97.3	248..	117.8	290..	138.9
123..	57.6	165..	77.6	207..	97.8	249..	118.4	291..	139.5
124..	58.1	166..	78.0	208..	98.3	250..	118.9	292..	139.9
125..	58.5	167..	78.5	209..	98.8	251..	119.3	293..	140.5
126..	59.1	168..	79.0	210..	99.3	252..	119.9	294..	140.9
127..	59.5	169..	79.5	211..	99.7	253..	120.3	295..	141.5
128..	60.0	170..	79.9	212..	100.3	254..	120.9	296..	142.0
129..	60.4	171..	80.4	213..	100.7	255..	121.3	297..	142.5
130..	60.9	172..	80.9	214..	101.2	256..	121.8	298..	143.0
131..	61.4	173..	81.4	215..	101.8	257..	122.4	299..	143.5
132..	61.8	174..	81.9	216..	102.2	258..	122.8	300..	144.0
133..	62.3	175..	82.3	217..	102.7	259..	123.4	301..	144.5
134..	62.7	176..	82.8	218..	103.1	260..	123.8	302..	145.0
135..	63.3	177..	83.3	219..	103.7	261..	124.3	303..	145.5
136..	63.8	178..	83.8	220..	104.0	262..	124.8	304..	146.0
137..	64.2	179..	84.3	221..	104.6	263..	125.3	305..	146.6
138..	64.7	180..	84.7	222..	105.2	264..	125.9	306..	147.0
139..	65.1	181..	85.2	223..	105.6	265..	126.3	307..	147.6
140..	65.6	182..	85.6	224..	106.1	266..	126.8	308..	148.0
141..	66.1	183..	86.2	225..	106.6	267..	127.3	309..	148.6
142..	66.5	184..	86.7	226..	107.1	268..	127.8	310..	149.0
143..	67.1	185..	87.1	227..	107.5	269..	128.3	311..	149.6
144..	67.5	186..	87.6	228..	108.0	270..	128.8	312..	150.0
145..	68.0	187..	88.0	229..	108.5	271..	129.4	313..	150.6
146..	68.4	188..	88.6	230..	109.0	272..	129.8	314..	151.1
147..	68.9	189..	89.1	231..	109.5	273..	130.3	315..	151.6
148..	69.4	190..	89.5	232..	110.0	274..	130.8	316..	152.1
149..	69.9	191..	90.0	233..	110.5	275..	131.4	317..	152.6
150..	70.3	192..	90.5	234..	111.0	276..	131.8	318..	153.1
151..	70.8	193..	91.0	235..	111.5	277..	132.4	319..	153.6

Milligrams copper.	Milligrams starch or dextrin.	Milligrams copper.	Milligrams starch or dextrin.	Milligrams copper.	Milligrams starch or dextrin.	Milligrams copper.	Milligrams starch or dextrin.	Milligrams copper.	Milligrams starch or dextrin.
320..	154.1	349..	169.0	378..	184.3	407..	199.6	436..	215.2
321..	154.7	350..	169.6	379..	184.7	408..	200.1	437..	215.7
322..	155.1	351..	170.1	380..	185.3	409..	200.7	438..	216.3
323..	155.7	352..	170.6	381..	185.8	410..	201.2	439..	216.8
324..	156.1	353..	171.1	382..	186.3	411..	201.8	440..	217.4
325..	156.7	354..	171.6	383..	186.9	412..	202.3	441..	217.9
326..	157.2	355..	172.1	384..	187.4	413..	202.8	442..	218.5
327..	157.7	356..	172.7	385..	188.0	414..	203.3	443..	219.1
328..	158.2	357..	173.2	386..	188.4	415..	203.9	444..	219.6
329..	158.7	358..	173.8	387..	189.0	416..	204.4	445..	220.2
330..	159.2	359..	174.2	388..	189.5	417..	205.0	446..	220.6
331..	159.8	360..	174.8	389..	190.0	418..	205.4	447..	221.2
332..	160.3	361..	175.4	390..	190.5	419..	206.0	448..	221.7
333..	160.8	362..	175.8	391..	191.1	420..	206.5	449..	222.3
334..	161.3	363..	176.4	392..	191.6	421..	207.1	450..	222.8
335..	161.8	364..	176.9	393..	192.1	422..	207.6	451..	223.4
336..	162.4	365..	177.5	394..	192.6	423..	208.2	452..	223.9
337..	162.8	366..	177.9	395..	193.2	424..	208.7	453..	224.4
338..	163.4	367..	178.5	396..	193.8	425..	209.3	454..	225.0
339..	163.9	368..	179.0	397..	194.3	426..	209.8	455..	225.6
340..	164.4	369..	179.5	398..	194.8	427..	210.3	456..	226.0
341..	165.0	370..	180.0	399..	195.3	428..	210.9	457..	226.6
342..	165.4	371..	180.6	400..	195.9	429..	211.4	458..	227.1
343..	166.0	372..	181.1	401..	196.4	430..	212.0	459..	227.7
344..	166.4	373..	181.6	402..	197.0	431..	212.5	460..	228.3
345..	167.0	374..	182.1	403..	197.4	432..	213.1	461..	228.8
346..	167.5	375..	182.7	404..	197.9	433..	213.6	462..	229.4
347..	168.0	376..	183.2	405..	198.5	434..	214.2	463..	230.0
348..	168.5	377..	183.7	406..	199.1	435..	214.7		

### THE PROTEIDS OF LUPIN SEEDS.<sup>1</sup>

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THE lupin is a leguminous plant little known in this country except as a garden ornament. The yellow lupin (*Lupinus luteus*) and the blue lupin (*Lupinus angustifolius*), both native to Mediterranean regions, have long been cultivated in Europe because of their ability to grow luxuriantly on sandy or gravelly soils, and by their help large areas of poor, "worn out" land have been reclaimed and made agriculturally profitable, as these plants furnish abundant fodder and by the decay of their deeply penetrating roots, and especially when plowed under

<sup>1</sup> From the Report of the Connecticut Agricultural Experiment Station for 1896.

green, they rapidly impregnate the soil with humus and render it productive for other crops.

Ritthausen<sup>1</sup> first studied and described under the name *conglutin*, the characteristic proteid of the lupin seed. He found that the yellow and the blue lupin both yielded conglutin scarcely distinguishable in properties and only differing in composition as respects sulphur, of which his preparations from the yellow lupin contained one per cent. and those from the blue lupin but one-half per cent. Ritthausen also analyzed preparations which, from their composition, he concluded to be legumin. He stated that both legumin and conglutin are extracted from lupin seeds by salt solutions as well as by dilute alkali, and that the two proteids can be separated from each other by dissolving in alkali, then precipitating with an acid and finally treating with salt solution. On neutralizing these alkali solutions conglutin retains, while legumin loses its solubility in saline solutions.

By extracting with five per cent. sodium chloride brine Ritthausen obtained two preparations from yellow lupin having the composition given under 1 and 2; by dissolving 2 in potash water and reprecipitating, 3 was prepared; the blue lupin by extracting with salt solution yielded 4.

## CONGLUTIN, RITTHAUSEN.

	Yellow Lupin.			Blue Lupin.
	1	2	3	4
Carbon.....	50.40	50.58	50.26	50.39
Hydrogen.....	7.00	7.06	6.89	6.94
Nitrogen.....	18.34	18.04	18.28	18.22
Sulphur } .....	24.26	24.32	{ 1.01	0.49
Oxygen } .....			{ 23.56	23.96
	<hr/> 100.00	<hr/> 100.00	<hr/> 100.00	<hr/> 100.00

The proteid rendered insoluble in salt solution by previous precipitation from an alkaline liquid, by acetic acid, he found to have the following composition, these figures being the average of five quite closely agreeing analyses :

## LEGUMIN, RITTHAUSEN.

Carbon .....	51.36
Hydrogen .....	6.97
Nitrogen .....	17.50
Sulphur.....	0.59
Oxygen .....	23.58
	<hr/> 100.00

<sup>1</sup> *J. prakt. Chem.*, 103, 78: *Ibid*, New Series, 24, 222, and 26, 422, and *Die Eiweisskörper*, etc., Bonn, 1872.

Palladin<sup>1</sup> has recently described the properties of "vitellin" contained in seeds of the yellow lupin. In many details the results of his work do not agree with ours, but as he admits that the "vitellin" which he examined was always somewhat impure, it is unnecessary to review his statements here.

#### YELLOW LUPIN.

We find that seeds of the yellow lupin contain a small quantity of proteid that is soluble in pure water, a large quantity soluble in salt solutions, a small amount soluble in potash water, and a little nitrogenous matter, presumably proteid, which cannot be extracted by these solvents.

To determine the proportions of these proteids, very finely ground yellow lupin meal was first completely extracted with warm alcohol of 0.868 sp. gr. in order to remove, as far as possible, the amides and alkaloids which occur in considerable quantities in this seed. The air-dried meal before exhaustion with alcohol contained 8.16 per cent. of nitrogen. Alcohol removed eleven per cent. of the meal and gave a residue containing 8.49 per cent. of nitrogen, showing that six-tenths per cent. of nitrogen calculated on the original meal had been removed. The original meal accordingly contained 7.56 per cent. of nitrogen in the form of compounds insoluble in alcohol. As the seed reacted strongly acid towards litmus it is possible that a considerable quantity of alkaloids was not removed by the alcohol, but it was not desirable to add any alkali in this extraction for fear of affecting the proteids.

One thousand grams of the alcohol-exhausted and thoroughly air-dried meal were treated with successive quantities of ten per cent. sodium chloride solution until saturation of the filtered extract with ammonium sulphate showed that no more proteid was removed. The united extracts were filtered clear and saturated with ammonium sulphate; the precipitated proteids were dissolved in brine and the solution filtered and dialyzed for several days. The abundant precipitate thus produced was filtered out, washed by decantation with water and with alcohol and dried over sulphuric acid. The substance thus obtained weighed 279 grams.

The solution filtered from this globulin was saturated with

<sup>1</sup> *Ztschr. fur. Biol.*, 31, 191.



ammonium sulphate, the precipitate produced was dissolved in water and the solution filtered and dialyzed until no more globulin separated. By this second dialysis 15.2 grams of globulin were secured. The solution filtered from this second portion of globulin was concentrated by dialyzing in alcohol and the proteid completely thrown down by adding absolute alcohol. The precipitate which resulted was then dehydrated with absolute alcohol and dried over sulphuric acid. Only 4.20 grams of substance were thus obtained, indicating the presence of very little proteid soluble in water.

The residue of meal was washed with water, which took up no proteid, and exhausted by successive applications of two-tenths per cent. potash water. The alkaline extracts were filtered clear and treated with dilute acetic acid. No precipitate resulted until a decided excess of acid had been added. The proteid thus separated was washed with water and with alcohol, dried over sulphuric acid and weighed 60.53 grams.

The meal residue was next washed with water and with alcohol, dehydrated with absolute alcohol and thoroughly air-dried. It weighed 192.0 grams, showing the lupin seed to contain over eighty per cent. of substance soluble in salt solution and very dilute alkali, an amount not approached by any other seed which we have examined.

The nitrogen was determined in the various products and the results are summarized in the following table :

AMOUNT OF PROTEID EXTRACTED FROM YELLOW LUPIN BY VARIOUS SOLVENTS.			Grams.
Extracted residue contained 1.51 per cent. N. or .....			2.90
Proteid extracted by alkali, 60.53 grams, contained 16.43			
		per cent. N. or .....	9.95
Proteid extracted by salt solution {	279.0 grams, contained 17.86		
		per cent. N. or ....	49.83
	15.2 grams, contained 18.09		
		per cent. N. or ....	2.75
Proteid extracted by water, 4.2 grams, contained 16.55			
		per cent. N. or ....	0.69
Total proteid, 358.93 grams.			
Total nitrogen accounted for .....			66.12
1,000 grams of meal contained 8.49 per cent. N. or .....			84.90

We thus have 77.88 per cent. of the nitrogen accounted for.

We will next consider in order :

- I. Proteids soluble in pure water.
- II. Proteids insoluble in water, but soluble in sodium chloride solution.
- III. Proteids insoluble in water and in salt solution, but soluble in dilute potash water.

#### *I. Proteids Soluble in Pure Water.*

As just indicated, water-soluble proteids occur in yellow lupin seeds in very small amount. Much the largest quantity obtained in any of the numerous extractions made was that already described, which formed 0.42 per cent. of the alcohol-extracted meal or 0.37 per cent. of the original meal. On treating this substance with water, a very considerable part was found to be coagulated. Since proteoses are not supposed to be rendered insoluble by prolonged treatment with alcohol, this insoluble matter was probably coagulated albumin or globulin, or possibly a mixture of both. The aqueous solution filtered from this insoluble proteid yielded a very small flocculent coagulum at 59°. The solution filtered after heating to 65°, became turbid at 67°, and flocks in minute amount appeared at 69°, which steadily increased until at 85° a very considerable coagulum had formed.

In another extraction by means of water, prolonged dialysis caused the separation of a small quantity of globulin which, when dissolved in salt solution, yielded a flocculent coagulum at 59° and but traces above 65°.

The solution from which most of this globulin had been removed by dialysis, gave a slight coagulum at 59°, and after heating to 65° the filtrate became turbid at 66°, and at 84° again yielded a small flocculent coagulum.

It is probable, therefore, that the substance coagulating at 59° is a globulin soluble in extremely dilute salt solutions which it is impossible to separate completely by dialysis and that the proteid coagulating at the higher temperature is an albumin.

Owing to the exceedingly small quantity of these proteids nothing further was learned respecting them.

The solution from which the coagulated proteid had been removed by heating gave a strong rose-red reaction with the

biuret test, but no precipitate in the cold with nitric acid even after adding salt.

The yellow lupin seed accordingly contains a very small amount of albumin and a small quantity of proteose.

Neumeister<sup>1</sup> states that he found peptone in lupin seeds in large amount.

In order to test the seeds of the yellow lupin for peptones, 1,000 grams of freshly ground meal were treated with three liters of distilled water, and after agitating therewith for an hour the extract was strained through fine bolting-cloth and the residue pressed out in a powerful screw press. Two liters of extract rich in dissolved substances was obtained, which was immediately saturated with ammonium sulphate and filtered. Lest peptones might be formed during the operation of extraction, the process up to this point was carried forward as rapidly as possible so that not over three hours elapsed before the solution, saturated with ammonium sulphate, was filtered. In order to be sure that the solution had been thoroughly saturated, a quantity of crystals of this salt were suspended in it over night, but no more proteid separated. Neumeister has stated that saturating seed extracts while hot and when made alternately acid and alkaline in reaction, is unnecessary. We, however, heated the solution to boiling, added ammonium sulphate as long as it dissolved, concentrated somewhat and allowed to cool. Much ammonium sulphate separated, but no noticeable quantity of proteose. After filtering off the separated sulphate, the solution was heated to boiling and concentrated until sulphate began again to crystallize out. Ammonia was next added to distinct alkaline reaction, and after heating a short time the solution was again cooled, filtered from deposited sulphate, and the filtrate concentrated until more sulphate separated. Acetic acid was added to acid reaction, the heating continued for a time, and the whole again cooled. After filtering out the separated crystals the solution measured 350 cc. The solution was then nearly neutralized with ammonia, leaving its reaction slightly acid, and after adding an equal volume of water a freshly prepared solution of tannic acid was gradually added so long as a precipitate was produced in a small portion of the filtered liquid. A bulky reddish precipitate

<sup>1</sup> *Ztschr. für. Biol.*, n. f., 12, 461.

formed which, after standing twenty-four hours, was removed from the filter and treated with a slight excess of hot concentrated solution of baryta. After standing a short time the warm solution was filtered, and as it was very strongly alkaline from free ammonia, one-half was neutralized with sulphuric acid, thereby removing the excess of baryta. Neutral lead acetate was then added and the solution filtered. The most carefully applied biuret test did not show the least trace of peptone in this solution. The remainder was then evaporated nearly to dryness and about two cc. of syrup obtained which, if it had all been peptone, would hardly be considered a large amount. No peptone reaction whatever could be obtained with this syrup.

The other half of the solution was treated exactly as Neumeister directed—that is, neutral lead acetate was added without neutralizing the ammonia, and, after filtering, the biuret reaction was applied, but with no indication of peptone.

Since writing the above, S. Frankfurt<sup>1</sup> has stated that no peptone is present in seeds of the lupin, and attributes Neumeister's results to his long treatment of the seeds with water. In a letter to Frankfurt, Neumeister stated that after swelling the seeds in water they were rubbed up and digested with water for twenty-four hours, and that the vessels containing the extracting seeds were exposed to the direct action of sunlight in summer. It is thus evident that the peptone found by Neumeister was formed during the extraction and was not an original constituent of the seed.

## II. *Proteids Soluble in Saline Solutions.*

As just mentioned, a very small quantity of a globulin soluble in extremely dilute salt solutions, yielding a flocculent coagulum when its solution in ten per cent. sodium chloride is heated to 59°, was found in extracts of the yellow lupin seed. As but little of this proteid is present in this seed, no attempt was made to do more than note its presence. Owing to its ready solubility in very dilute salt solutions, this proteid dissolves when lupin meal is treated with water. Besides this little if any other globulin substance is extracted from lupin seeds by the dilute saline solution which results when the meal is treated with water. Large

<sup>1</sup> *Landw. Ver.-Stat.*, 47, 454.

quantities of globulin are, however, obtained by extraction with stronger salt solutions.

One hundred grams of meal yielded directly with salt solution an extract which was filtered clear, saturated with ammonium sulphate, the precipitate produced filtered out, dissolved in brine, and the solution filtered clear and dialyzed for eighteen hours. The globulin thus precipitated was filtered out, washed with water, alcohol, and ether, dried over sulphuric acid, and found to weigh twelve grams. The filtrate by further dialysis similarly yielded four and seven-tenths grams of globulin. These preparations, 1 and 2, were analyzed with the results given below. The residue, remaining after exhausting 100 grams of meal with water, on treating with salt solution gave an extract which, when filtered clear and dialyzed four days, yielded 20.36 grams of globulin, preparation 3, having the composition given in the following table. A large quantity of the globulin was prepared by extracting one kilogram of finely ground lupin meal with six liters of brine, filtering the resulting solution, saturating with ammonium sulphate, filtering out the precipitate produced, dissolving this in dilute salt solution, again precipitating by saturating with ammonium sulphate, redissolving the precipitate, filtering the solution so obtained and dialyzing for forty hours. The very large precipitate which separated was washed thoroughly by decantation with water, dilute alcohol, absolute alcohol and ether and then dried over sulphuric acid. In this way 112 grams of preparation 4 were secured having the composition given in the subjoined table. The filtrate from 4, after three days further dialysis, gave a second precipitate of globulin which was decidedly more viscid than 4. This by the usual treatment yielded 30 grams of preparation 5 with the composition given below.

Another portion of meal weighing one kilogram was several times extracted with water and the residue treated with successive applications of ten per cent. salt solution. The extract was filtered clear and dialyzed for forty hours. The globulin so precipitated was thoroughly washed with water by decantation, then with dilute alcohol and then with absolute alcohol until no more color was removed, and finally with ether and then dried over sulphuric acid; 120 grams of preparation 6 were thus

obtained, giving on analysis the figures stated below. The solution from which 6 had separated was saturated with ammonium sulphate, the precipitate dissolved in brine and the solution returned to the dialyzer. After some days the small precipitate which had separated was filtered out, washed and dried in the usual manner and gave five grams of preparation 7 having the composition given below.

In order to avoid as far as possible any contamination of the proteid with nitrogenous or other substances soluble in alcohol, a quantity of very fine ground lupin meal was exhausted in Squibb's percolator with a large quantity of strong alcohol, the process being continued until only a trace of solid matter remained after evaporating a considerable quantity of the alcoholic extract.

Two kilograms of this meal were then extracted as thoroughly as possible with brine, the solution filtered clear and saturated with ammonium sulphate. The proteids thus precipitated were dissolved in brine, the solution filtered perfectly clear and the globulin thrown down by dialyzing three days was filtered off, washed and dried in the manner already described. There was thus obtained 506 grams of globulin, preparation 8.

The solution filtered from 8 by longer dialysis yielded forty-five grams of preparation 9. These preparations had the composition given below.

## LUPIN GLOBULIN.

	1.	2.	3.	4.	5.	6.	7.	8.	9.
Carbon .....	50.62	50.68	50.63	50.49	50.29	50.41	49.81	50.20	49.47
Hydrogen ..	6.94	6.95	7.00	6.77	6.89	6.85	6.79	6.75	6.77
Nitrogen ...	17.45	17.89	18.05	17.90	17.88	18.01	17.79	17.86	18.07
Sulphur ....	0.77	0.80	0.88	0.88	1.25	0.87	1.48	0.98	1.49
Oxygen.....	24.22	23.68	23.44	23.96	23.69	23.86	24.13	24.21	24.20
	<u>100.00</u>	<u>100.00</u>	<u>100.00</u>	<u>100.00</u>	<u>100.00</u>	<u>100.00</u>	<u>100.00</u>	<u>100.00</u>	<u>100.00</u>
Ash.....	0.51	0.27	0.74	0.26	0.30	0.99	0.83	0.38	0.23

These figures agree quite closely except those for 5, 7, and 9 in which carbon is less and sulphur decidedly more than in the others. The fact that these three preparations separated on prolonged dialysis of the solutions which had yielded 4, 6, and 8 indicates the presence of two globulins of different composition.

It was therefore necessary to submit this substance to very thorough fractional precipitation in order to determine definitely its true composition. Accordingly, 100 grams of preparation 6

were dissolved in 800 cc. of five per cent. salt solution, filtered from a very small quantity of insoluble matter, and the perfectly clear solution was mixed with 800 cc. of water and cooled to 0°. A very large proportion of the dissolved proteid separated as a solid, coherent mass on the bottom of the beaker, from which the clear solution was completely decanted. This precipitate was marked *A*, the solution *B*. The precipitate *A* was dissolved in 100 cc. of ten per cent. brine, yielding readily a perfectly clear solution. This was mixed with 100 cc. of water at 20° but no precipitate resulted. Water was then added gradually until an abundant precipitate formed and the total volume equalled 500 cc. After settling, the clear solution was poured off from the precipitate and the latter washed thoroughly with water and alcohol and dried over sulphuric acid. In this way 46 grams of preparation 10 were obtained, having the following composition :

## LUPIN GLOBULIN, 10.

Carbon .....	50.49
Hydrogen .....	6.77
Nitrogen .....	17.89
Sulphur.....	0.66
Oxygen .....	24.19
	<hr/>
	100.00
Ash .....	0.51

The solution decanted from 10 was mixed with 600 cc. more water, which gave another precipitate that, after washing and drying, weighed ten and a half grams and had the composition given below.

## LUPIN GLOBULIN, 11.

Carbon .....	50.18
Hydrogen .....	6.94
Nitrogen .....	17.93
Sulphur....	0.82
Oxygen .....	24.13
	<hr/>
	100.00
Ash .....	0.77

The solution *B* decanted from the first precipitate *A*, as described above, was diluted with an equal volume of water, cooled to 0°, and allowed to deposit the resulting precipitate. After washing and drying, preparation 12, weighing eight

grams, was obtained, which gave the following results on analysis :

## LUPIN GLOBULIN, 12.

Carbon .....	50.08
Hydrogen .....	6.82
Nitrogen .....	18.26
Sulphur .....	1.30
Oxygen .....	23.54
	<hr/>
	100.00
Ash .....	0.74

The solution from which 12 separated was saturated with ammonium sulphate, the proteid thereby precipitated was dissolved in water and the clear solution dialyzed. A small precipitate resulted, which when washed and dried, weighed one and four-tenths grams and had the following composition :

## LUPIN GLOBULIN, 13.

Carbon .....	49.54
Hydrogen .....	6.91
Nitrogen .....	18.24
Sulphur } .....	25.31
Oxygen }	
	<hr/>
	100.00
Ash .....	0.49

These fractional precipitations show a regular decrease in their content of carbon and an increase in both nitrogen and sulphur, that of the latter being especially marked. It is to be noted that the total weight of the foregoing fractions formed only 65.9 per cent. of the proteid taken, suggesting that the globulin was undergoing a change while in solution ; but as no especial care was exercised to obtain all the proteid from the solutions, this process was repeated, not only with a view to settling this point, but to obtain larger quantities of the extreme fractions for further examination.

One hundred grams of preparation 8 were dissolved in 800 cc. of five per cent. brine and the solution, after filtering perfectly clear, was mixed with 800 cc. of water, and cooled to 10°. The abundant precipitate which resulted was allowed to settle, and the solution decanted. The precipitate was marked *C*, the solution *D*. Precipitate *C* was next dissolved in 100 cc. of ten per cent. brine and 300 cc. of water at 20° added to the resulting



solution. After standing some time the clear solution was decanted from the large deposit of proteid and the latter washed and dried. Thus were obtained fifty grams of preparation 14, which analysis showed to have the following composition :

## LUPIN GLOBULIN, 14.

Carbon.....	50.71
Hydrogen.....	7.00
Nitrogen.....	17.86
Sulphur.....	0.67
Oxygen.....	23.76
	<hr/>
	100.00
Ash.....	0.39

The filtrate from 14 was mixed with 400 cc. of the first washings of 14 and cooled to 7°–8°. On standing, a part of the proteid deposited and the clear solution was then decanted. The precipitate, preparation 15, after washing and drying weighed 8.46 grams, and according to analysis contained :

## LUPIN GLOBULIN, 15.

Carbon.....	50.14
Hydrogen.....	6.94
Nitrogen.....	17.83
Sulphur.....	0.86
Oxygen.....	24.23
	<hr/>
	100.00
Ash.....	0.81

The solution from which 15 had separated was dialyzed, but only a very small quantity of globulin could be obtained, preparation 16, which weighed seven-tenths gram and without correction for ash contained 18.22 per cent. of nitrogen. Solution *D* decanted from precipitate *C*, as already described, was cooled to 3°, that is, 7° lower than before. This caused a further quantity of globulin to separate, which gave preparation 17, weighing 21.14 grams.

## LUPIN GLOBULIN, 17.

Carbon.....	50.13
Hydrogen.....	6.88
Nitrogen.....	17.72
Sulphur.....	0.80
Oxygen.....	24.47
	<hr/>
	100.00
Ash.....	0.59

The solution from which 17 separated was dialyzed free from chlorides and 13.7 grams of preparation 18 obtained, having the following composition :

## LUPIN GLOBULIN, 18.

Carbon.. .. .	50.04
Hydrogen .. . . .	6.79
Nitrogen .. . . .	18.43
Sulphur.....	1.48
Oxygen .. . . .	23.26
	<hr/>
	100.00
Ash .. . . .	0.25

The filtrate from 18 contained but a very little proteid precipitable with ammonium sulphate. The total weight of these fractions was ninety-four grams ; the six grams unaccounted for may be fairly attributed to mechanical loss and therefore a change of proteid to non-proteid substances is improbable.

These fractions, like those of the preceding series, show a decrease in carbon and an increase in nitrogen and sulphur as we pass from the least to the most soluble.

Another series of separations was next made by fractional solution.

One hundred grams of preparation 8 were dissolved in 800 cc. of five per cent. brine diluted with 800 cc. of water at 20° and the solution cooled to 5°. The clear solution was then decanted from the separated proteid and dialyzed till free from chlorine. The globulin thus separated after washing and drying weighed 24.03 grams and had the following composition :

## LUPIN GLOBULIN, 19.

Carbon.....	50.11
Hydrogen .. . . .	6.84
Nitrogen .. . . .	18.46
Sulphur.....	1.28
Oxygen .. . . .	23.31
	<hr/>
	100.00
Ash .. . . .	0.17

The proteid deposited by cooling, as just described, was dissolved in 700 cc. of five per cent. brine and cooled at 5°. The clear solution was decanted and dialyzed, yielding 18.60 grams of preparation 20, which contained :

## LUPIN GLOBULIN, 20.

Carbon.....	50.27
Hydrogen .....	6.78
Nitrogen .....	18.43
Sulphur.....	1.15
Oxygen .....	23.37
	<hr/>
	100.00
Ash .....	0.10

The substance precipitating on cooling, as just described, was dissolved in 600 cc. of five per cent. salt solution, mixed with an equal volume of water, and cooled to 2°. The clear solution was dialyzed and five and six-tenths grams of preparation 21 were obtained, which gave the following results on analysis :

## LUPIN GLOBULIN, 21.

Carbon.....	50.03
Hydrogen .....	6.86
Nitrogen .....	18.47
Sulphur.....	1.49
Oxygen .....	23.15
	<hr/>
	100.00
Ash .....	0.22

The precipitate that separated on cooling the solution from which 21 was obtained, was dissolved in 500 cc. of five per cent. brine, diluted with an equal volume of water, and cooled to 7°. The solution was decanted from the precipitate and dialyzed. Thus was obtained 4.31 grams of preparation 22, which contained :

## LUPIN GLOBULIN, 22.

Carbon.....	50.44
Hydrogen .....	6.92
Nitrogen .....	18.23
Sulphur.....	1.14
Oxygen .....	23.27
	<hr/>
	100.00
Ash .....	0.11

The substance deposited by cooling, as last described, was dissolved in 300 cc. of five per cent. salt solution, filtered clear and dialyzed till free from chlorides. The deposited globulin, after washing and drying, weighed 33.88 grams and contained :

## LUPIN GLOBULIN, 23.

Carbon.....	51.13
Hydrogen .....	6.86
Nitrogen .....	18.03
Sulphur.....	0.49
Oxygen .....	23.49
	<hr/>
	100.00
Ash .....	0.52

Like the preceding, this series of fractional separations shows a decrease in carbon and an increase in nitrogen and sulphur with increased solubility. The total weight of the fractions obtained was 86.42 grams, the loss being no greater than was to be expected.

Thirty-five grams of preparation 10 and the same quantity of preparation 14, representing the least soluble portions obtained in the two first series of fractions, were next dissolved in 600 cc. of five per cent. brine, diluted with an equal volume of water, and cooled to 6°. The solution was decanted from the precipitate which resulted, filtered clear, and dialyzed. The globulin thus precipitated after washing and drying weighed 12.43 grams and contained :

## LUPIN GLOBULIN, 24.

Carbon.....	50.10
Hydrogen .....	6.94
Nitrogen .....	18.12
Sulphur.....	0.94
Oxygen .....	23.90
	<hr/>
	100.00
Ash .....	0.23

The precipitate produced by cooling the solution, as just described, was dissolved in 500 cc. of salt solution, diluted with 500 cc. of water and cooled to 6°. The deposited proteid, after the usual treatment, weighed 7.80 grams and had the following composition :

## LUPIN GLOBULIN, 25.

Carbon.....	50.32
Hydrogen .....	6.90
Nitrogen .....	18.06
Sulphur.....	0.81
Oxygen .....	23.91
	<hr/>
	100.00
Ash .....	0.27

The substance separated by cooling, as just described, was dissolved in one liter of two and one-half per cent. sodium chloride solution and cooled to 7°. The clear liquid, decanted from the thus precipitated proteid, was dialyzed and yielded 5.51 grams of globulin, giving, on analysis, the following results :

## LUPIN GLOBULIN, 26.

Carbon.....	50.80
Hydrogen .....	6.91
Nitrogen .....	18.01
Sulphur.....	0.64
Oxygen .....	23.64
	<hr/>
	100.00
Ash .....	0.23

The proteid separated by cooling the solution from which 26 had been obtained was dissolved in half a liter of five per cent. salt solution, diluted with an equal volume of water, and cooled to 14°. The clear solution was decanted and dialyzed and gave four and nine-tenths grams of preparation 27, which analysis showed to have the composition here given :

## LUPIN GLOBULIN, 27.

Carbon.....	50.90
Hydrogen .....	6.85
Nitrogen .....	17.88
Sulphur.....	0.55
Oxygen .....	23.82
	<hr/>
	100.00
Ash .....	0.27

The substance deposited at 14°, as noted above, was dissolved in half a liter of five per cent. brine, diluted to one liter, and allowed to settle at the temperature of the room (about 22°). The liquid was then decanted, dialyzed, and further treated in the usual manner. There was thus obtained 5.45 grams of preparation 28, which contained :

## LUPIN GLOBULIN, 28.

Carbon.....	50.93
Hydrogen .....	6.94
Nitrogen .....	17.83
Sulphur.....	0.48
Oxygen .....	23.82
	<hr/>
	100.00
Ash .....	0.23

The substance separated by diluting the solution from which 28 resulted, was washed with water and alcohol, dried, and found to weigh 20.6 grams. Its composition was :

LUPIN GLOBULIN, 29.	
Carbon .....	50.80
Hydrogen .....	6.83
Nitrogen .....	17.88
Sulphur.....	0.46
Oxygen .....	24.03
	<hr/>
	100.00
Ash .....	0.70

This, like the other series of fractional separations, shows an increase in carbon and decrease in sulphur and nitrogen content accompanying a decrease in solubility. If the final fractions, which have been most thoroughly purified, are arranged as in the table below, it will be seen that a nearly constant composition has been reached so that the average of these analyses may be taken as closely representing the composition of the least soluble and most abundant globulin of the yellow lupin.

	YELLOW LUPIN GLOBULIN, CONGLUTIN.					
	23.	26.	27.	28.	29.	Average.
Carbon ....	51.13	50.80	50.90	50.93	50.80	50.91
Hydrogen..	6.86	6.91	6.85	6.94	6.83	6.88
Nitrogen ..	18.03	18.01	17.88	17.83	17.88	17.93
Sulphur ...	0.49	0.64	0.55	0.48	0.46	0.52
Oxygen....	23.49	23.64	23.82	23.82	24.03	23.76
	<hr/>	<hr/>	<hr/>	<hr/>	<hr/>	<hr/>
	100.00	100.00	100.00	100.00	100.00	100.00

This is the globulin discovered by Ritthausen, and described by him under the name conglutin.

A careful examination of preparation 29 showed this globulin to have the following reactions :

In very dilute acids and alkalies it is completely soluble, yielding perfectly clear solutions of a light yellow color.

Dissolved in very dilute acetic acid, the proteid is precipitated by neutralizing the solution with sodium carbonate. On adding sodium chloride brine to the solution containing the precipitate in suspension, the latter is completely dissolved.

In ten per cent. sodium chloride brine it dissolves readily, giving a very slight turbid solution of a pale yellow color, which

turns litmus paper red, lacmoid paper blue, and has no effect on tropæoline when evaporated to dryness with it.

A solution containing ten per cent. of the globulin dissolved in ten per cent. sodium chloride brine behaved as follows :

Dilution with twice its volume of water produced a considerable precipitate.

Addition of one drop of acetic acid, sp. gr. 1.035, or one drop of hydrochloric acid (one part concentrated acid and three parts of water) to five cc. of this solution gave a heavy precipitate.

Addition of mercuric chloride<sup>1</sup> dissolved in ten per cent. brine gave no precipitate.

Tannin as well as picric acid gave a heavy precipitate.

Diluted with an equal volume of ten per cent. brine the solution, containing five per cent. of globulin, reacted as follows :

No precipitate was produced by saturation with sodium chloride, magnesium sulphate or sodium sulphate at 20°, but at 34° saturation with the last named salt precipitated all but a minute trace of the globulin.

When the solution in ten per cent. sodium chloride brine, containing five per cent. of proteid, was heated gradually in a water-bath, no change appeared even after heating some time at 100°. After more prolonged heating a thick transparent skin formed on the surface. On cooling and standing several hours, the solution set to a solid jelly and became somewhat turbid.

Addition of nitric acid to the solution in brine gave a precipitate not soluble in an excess of this acid. On heating, the usual xanthoproteic reaction occurred, which was preceded by the development of a slight pink color quickly changing to yellow, doubtless due to a trace of coloring matter still adhering to the proteid. When the globulin in the dry state was treated with very dilute nitric acid a clear solution resulted which gave a heavy precipitate on adding an excess of acid, that behaved on heating as just described. The usual proteid reactions were obtained with Millon's, Adamkiewics', and the biuret tests.

In order to determine the composition of the more soluble fractions, the greater parts of 18, 19, and 20 were united, giving

<sup>1</sup> Palladin (Ztschr. für Biol., 31, 195) states that ten per cent. sodium chloride solutions are not precipitated by mercuric chloride, but that diluted solutions give precipitates soluble in salt solution. The precipitate which he thus obtained was of course caused by the water added with the mercuric chloride. If he had dissolved the mercury salt in brine, no precipitate would have resulted.

forty grams of substance which was dissolved in 400 cc. of five per cent. brine, the solution was filtered perfectly clear, the filter washed with 100 cc. of the same salt solution, and the filtrate and washings were mixed with an equal volume of water. After cooling to 8°, and standing some time, a part of the globulin separated. From this the solution was decanted. The proteid was deposited as a viscid transparent fluid, which became opaque on treating with distilled water and finally solid. It was dehydrated with absolute alcohol and dried over sulphuric acid, giving 19.2 grams of preparation 30, having the following composition :

LUPIN GLOBULIN, 30.	
Carbon.....	49.64
Hydrogen .....	6.87
Nitrogen .....	18.21
Sulphur.....	1.20
Oxygen . . . . .	24.08
	<hr/>
	100.00
Ash .....	0.32

The solution decanted from preparation 30 was mixed with 500 cc. of water and cooled to 7°. The resulting precipitate, when treated in the same way as 30 had been, gave 9.25 grams of preparation 31, containing :

LUPIN GLOBULIN, 31.	
Carbon.....	49.62
Hydrogen .....	6.72
Nitrogen .....	18.22
Sulphur.....	1.36
Oxygen .....	24.08
	<hr/>
	100.00
Ash .....	0.43

The solution from which 31 had separated was dialyzed free from chlorides, and yielded seven and four-tenths grams of preparation 32 :

LUPIN GLOBULIN, 32.	
Carbon.....	49.59
Hydrogen .....	6.75
Nitrogen .....	18.43
Sulphur.....	1.62
Oxygen .....	23.61
	<hr/>
	100.00
Ash .....	0.17



These three fractions have very nearly the same composition, which is in close agreement with that of the other most soluble fractions already described, as may be seen from the following table :

LUPIN GLOBULIN.							
	13.	18.	9.	30.	31.	32.	Average.
Carbon . . . . .	49.54	49.63	49.47	49.64	49.62	49.59	49.58
Hydrogen . . .	6.91	6.78	6.77	6.87	6.72	6.73	6.80
Nitrogen . . . .	18.24	18.43	18.08	18.21	18.22	18.43	18.27
Sulphur .. } Oxygen . . . }	25.31	1.48 23.68	1.49 24.20	1.20 24.08	1.36 24.08	1.56 23.67	1.42 23.93
	<hr/> 100.00	<hr/> 100.00	<hr/> 100.00	<hr/> 100.00	<hr/> 100.00	<hr/> 100.00	<hr/> 100.00

A series of tests of preparation 30, conducted at the same time and under identical conditions with those described for preparation 29, revealed the following differences. In ten per cent. sodium chloride brine, 30 dissolved to a perfectly clear solution more colored than that yielded by 29.

Preparation 30, dissolved in brine to a solution containing ten per cent. both of salt and proteid, was not even rendered turbid by dilution with two volumes of water, but with three volumes a slight precipitate was given. A similar solution of 29, with two volumes of water, gave a considerable precipitate, and with three volumes a very heavy precipitate.

Five cc. of the ten per cent. solution of 30 required eight drops of acetic acid, sp. gr. 1.035, to produce a slight precipitate, while one drop under the same conditions gave a heavy precipitate in a similar solution of 29.

With one drop of hydrochloric acid (one part concentrated hydrochloric acid and three parts water) only a turbidity was produced in the case of 30, while under like conditions 29 yielded a heavy precipitate.

Saturation with sodium sulphate of the solution containing five per cent. of 30 gave only a partial precipitation, 29 being wholly precipitated under like conditions.

When this five per cent. solution in ten per cent. brine was heated in a water-bath a turbidity formed at 94°, increasing as the temperature was raised, becoming dense at 99°, and after long heating a gelatinous flocculent precipitate separated which was unchanged on cooling and standing ; when heated with

nitric acid the pink color which preceded the yellow of the xanthoproteic reaction was more pronounced than that yielded by 29.

In all other respects no difference could be detected between the reactions of 30 and 29. The most noticeable property in which both differ from nearly all other vegetable globulins is that neither yields insoluble products (the so-called "albuminates") when separated from solution. The only evidence of such a tendency noticed in the very large number of preparations made, was in some cases shown by the presence of a slight turbidity when precipitates were redissolved.

Both give solutions which react strongly acid with litmus. Titrated with standard ammonia, two grams of each of these globulins required the addition of ten milligrams of ammonia to cause an alkaline reaction with litmus.

Although the analyses of the final fractions of the more soluble globulin agree closely and their properties and reactions are quite alike, it seems to us doubtful if they represent a definite chemical species. The close physical and chemical resemblance between the least soluble substance and the most soluble, suggests that they are closely related. The distinct difference in some properties observed between the extreme products of fractional precipitation make it probable that a combination of some sort has taken place between the conglutin and other constituents of the seed.

As the lupin seed is unusually rich in soluble constituents, it would not be surprising if the proteid on precipitation carried down with it more or less of these substances which could be with difficulty separated afterwards. From the globulin of the blue lupin by fractional precipitation readily soluble products were obtained which however were wholly different in composition and quite distinct in reaction from the more soluble fractions of the yellow lupin globulin. The soluble fractions are possibly conglutin combined either chemically or mechanically with other constituents of the seed, which in the two varieties of lupin are apparently present in different proportions.

### III. *Proteid Insoluble in Water and Saline Solution but Soluble in Dilute Alkalies.*

As previously described on page 457 after exhausting one kilogram of yellow lupin meal with ten per cent. sodium chloride

solution and washing the residue with water, by continued extraction with two-tenths per cent. potash water a solution was obtained which after filtering clear and adding acetic acid to distinct acid reaction yielded a precipitate which after washing with water and alcohol and drying over sulphuric acid weighed 60.53 grams. This was redissolved in two-tenths per cent. potash water, the solution again filtered clear and carbon dioxide passed through it. The proteid partly separated, but could not be filtered, so a little ammonium chloride was added to convert the potassium carbonate into chloride, but even after passing carbon dioxide through the solution for some time and allowing it to stand over night in an ice box, only a partial separation resulted. Acetic acid was then added in slight excess and the precipitate filtered off and washed thoroughly with water and with alcohol. Dried at  $110^{\circ}$  this preparation, 33, gave the following results on analysis :

## LUPIN PROTEID, 33.

Carbon.....	51.40
Hydrogen .....	6.79
Nitrogen .....	16.43
Sulphur.....	1.03
Oxygen .....	24.35
	<hr/>
	100.00
Ash .....	1.57

## BLUE LUPIN.

One kilogram of fine ground meal of the seeds of the blue lupin was extracted with a large quantity of distilled water applied in successive portions and the residual meal thrown on fine bolting cloth after each application. The extract thus obtained was allowed to stand over night. The partly clarified liquid was siphoned off, saturated with ammonium sulphate, the precipitate dissolved in brine, and the solution filtered clear and dialyzed for forty-eight hours. A precipitate resulted which was filtered off, washed with water and with alcohol, and dried over sulphuric acid, giving preparation 34, weighing 8.46 grams. The filtrate was dialyzed for ten days longer in a stream of water, but no more proteid separated. The solution was then concentrated by dialysis in alcohol and absolute alcohol added until all the proteid contained in it was precipitated. The sub-

stance thus obtained weighed, when dry, only 1.42 grams and was not examined further than to find that it was nearly all insoluble in water, having been coagulated by the prolonged treatment with alcohol. This insolubility of the greater part of this substance shows that very little proteose is present.

Like the yellow lupin, this seed contains but little proteid matter soluble in water, and that is mostly globulin dissolved by aid of the salts extracted from the seed.

The meal residue which had been exhausted with water was treated with ten per cent. sodium chloride solution and the extract, after filtering perfectly clear, was dialyzed for forty hours. The globulin, which separated in a coherent mass on the bottom of the dialyzer, was washed thoroughly by decantation with water and with alcohol and dried over sulphuric acid. This gave 115.0 grams of preparation 35.

Another preparation of this globulin was made by treating one kilogram of the meal directly with ten per cent. brine, filtering the extract perfectly clear, and dialyzing for forty hours. The globulin thus precipitated, after washing and drying, formed preparation 36 and weighed 112 grams. These three preparations were dried at 110° and analyzed with the following results :

BLUE LUPIN GLOBULIN, CONGLUTIN.

	34.	35.	36.	Yellow lupin.
Carbon.....	50.58	50.82	50.85	50.91
Hydrogen.....	6.58	6.87	6.78	6.88
Nitrogen .....	17.82	18.04	18.04	17.93
Sulphur.....	0.72	0.40	0.50	0.52
Oxygen .....	24.30	23.87	23.83	23.76
	<hr/>	<hr/>	<hr/>	<hr/>
	100.00	100.00	100.00	100.00
Ash .....	0.64	1.22	1.11	

The agreement between 35 and 36 and the purified conglutin of the yellow lupin is very close indeed, but in order to be sure that this was not accidental these two preparations were subjected to the following treatment :

One hundred grams of 35 were dissolved in one-half liter of five per cent. sodium chloride brine and one-half liter of water added to the solution. A large rapidly settling precipitate resulted, which formed a semi-fluid mass on the bottom of the beaker, from which the very nearly clear solution *A* was poured

after a short time. The precipitate *B* was dissolved in 280 cc. of six and a half per cent. brine and the resulting solution, which measured 380 cc., was diluted with an equal volume of water and cooled to 5°. The solution was then decanted from the precipitate, which was washed and dried as usual and found to weigh 39.2 grams, preparation 37. The solution decanted from 37 was dialyzed until free from salt, whereby a precipitate resulted which, when washed and dried, weighed four and two-tenths grams and formed preparation 38. The solution *A*, decanted from precipitate *B*, as above described, was cooled to 5° and the solution *C* decanted from the precipitate *D*. This precipitate was again dissolved in 300 cc. of five per cent. brine, 300 cc. of water added, and the whole cooled to 5°. The precipitate thus produced, when dried, weighed 19.5 grams, preparation 39. The solution from which 39 had separated was dialyzed and yielded preparation 40, weighing five and four-tenths grams.

The solution *C* decanted from precipitate *D* was dialyzed free from chlorides and thereby thirteen grams of preparation 41 were separated. These preparations were dried at 110° and analyzed with the following results. In the table they are arranged according to their solubility in dilute salt solutions.

	37.	39.	38.	40.	41.
Carbon .....	51.25	51.04	50.82	50.98	50.79
Hydrogen .....	6.96	6.75	6.66	6.83	6.79
Nitrogen .....	18.11	18.15	17.69	17.66	17.64
Sulphur .....	0.32	0.24	0.49	0.38	0.39
Oxygen.....	23.36	23.82	24.34	24.15	24.39
	<hr/>	<hr/>	<hr/>	<hr/>	<hr/>
	100.00	100.00	100.00	100.00	100.00
Ash .....	0.95	0.71	0.61	0.52	0.75
Amount.. . .	39.2	19.5	4.2	5.4	13.0 grams

From these figures it would seem that preparation 35 contained some impurities, which accumulated in the three most soluble fractions in which the nitrogen is a little lower and the sulphur slightly higher than in the less soluble fractions. Preparation 36 was next fractionally precipitated in the following manner :

One hundred grams were dissolved in 700 cc. of five per cent. sodium chloride brine, filtered perfectly clear, and the solution diluted with an equal volume of distilled water. The proteid

separated as a viscid liquid from which the solution *E* was decanted. The precipitate *F* was dissolved in 100 cc. of five per cent. brine and the resulting solution, which measured 175 cc., was cooled in a freezing mixture to  $-4^{\circ}$ , and then allowed to stand until it had warmed to  $20^{\circ}$ . The precipitate thus produced formed a perfectly transparent syrupy liquid which measured 61 cc. The solution from which this had separated was decanted and the fluid precipitate was washed by stirring up with water, whereby it was rendered opaque and pasty. On washing with fresh quantities of water the substance became denser and granular. It was finally washed with alcohol and dried over sulphuric acid, giving twenty-five grams of preparation 42.

The washings of 42 were cooled to  $0^{\circ}$  and four-tenths gram of preparation 43 obtained. The solution from which this separated contained very little proteid, which was not saved. The solution *E*, decanted from precipitate *F*, was cooled to  $8^{\circ}$ , and the solution *G*, was decanted from the proteid *H*, thus separated.

This precipitate was treated with seventy-seven cc. of five per cent. sodium chloride brine giving a solution measuring 126 cc., which was cooled to  $-10^{\circ}$ , and then allowed to stand until warmed to  $20^{\circ}$ , when forty-nine cc. of a clear viscid liquid separated. This was washed with water in the same manner as 42 had been, and then with alcohol, dried over sulphuric acid, and 18.5 grams of preparation 44 obtained. From the washings of 44 by cooling to  $0^{\circ}$ , 2.62 grams of preparation 45 were separated. The solution *G*, decanted from precipitate *H*, was cooled in a freezing mixture until partly frozen, when it was allowed to melt and deposit the separated proteid. The latter, *J*, after decanting the solution *I*, was dissolved in fifty cc. of five per cent. sodium chloride brine and the seventy-five cc. of solution which resulted was cooled to  $-2^{\circ}$ , but only a turbidity resulted. The solution was therefore diluted with an equal volume of water, again cooled to  $-2^{\circ}$ , and slowly warmed to  $20^{\circ}$ . The proteid separated as a viscid liquid measuring twenty-four cc., and when washed with water and alcohol gave ten grams of preparation 46. From the washings of 46, by cooling to  $0^{\circ}$ , there separated 0.56 gram of preparation 47. The solution *I*,

decanted from precipitate *J*, was diluted with an equal volume of water, and cooled to 0°. The substance which separated was washed with water and alcohol and when dried weighed 9.15 grams, and formed preparation 48. The solution from which 48 had separated contained too little proteid to save.

Dried at 110° these preparations gave the following results on analysis, which are arranged in the table in the order of their solubility.

	42.	44.	43.	45.	46.	47.	48.
Carbon....	51.09	51.14	....	50.86	50.94	....	50.65
Hydrogen..	6.83	6.89	....	6.89	6.89	....	6.84
Nitrogen..	18.08	18.10	17.82+	17.95	17.79	17.77	17.56
Sulphur ..	0.38	0.33	....	0.46	0.27	....	0.44
Oxygen...	23.62	23.54	....	23.84	24.11	....	24.51
	<u>100.00</u>	<u>100.00</u>		<u>100.00</u>	<u>100.00</u>		<u>100.00</u>
Ash .....	0.59	0.47	?	0.69	0.51	0.54	0.86
Amount ..	25.00	18.50	0.40	2.62	10.00	0.56	9.15 gms.

If the analyses of preparations 37, 39, 42, and 44, which constitute the greater part of the proteid substance of 35 and 36, are compared it will be seen that they are in very close agreement, and it is fair to presume that they represent very nearly the true composition of this, the principal proteid of the blue lupin. If these analyses are also compared with those of conglutin from the yellow lupin, it will be evident that the two varieties of lupin contain one and the same globulin, especially since a rigid comparison of the reactions of purified preparations from the two seeds failed to reveal the slightest difference. The following table will facilitate a comparison of the above-mentioned figures:

CONGLUTIN.						
	Blue lupin.				Yellow lupin.	
	37.	39.	42.	44.	Average.	Average.
Carbon .....	51.25	51.04	51.09	51.14	51.13	50.91
Hydrogen....	6.96	6.75	6.83	6.89	6.86	6.88
Nitrogen....	18.11	18.15	18.08	18.10	18.11	17.93
Sulphur .....	0.32	0.24	0.38	0.33	0.32	0.52
Oxygen.....	23.36	23.82	23.62	23.54	23.58	23.76
	<u>100.00</u>	<u>100.00</u>	<u>100.00</u>	<u>100.00</u>	<u>100.00</u>	<u>100.00</u>

If now we compare the analyses of the more soluble fractions, as shown in the following table, they will be seen to be quite

similar to each other but decidedly different from the more soluble globulin of the yellow lupin :

	38.	40.	41.	46.	47.	48.	Average.	Soluble globulin yellow lupin.
Carbon . . .	50.82	50.98	50.79	50.94	....	50.65	50.84	49.58
Hydrogen.	6.66	6.83	6.79	6.89	....	6.84	6.80	6.80
Nitrogen .	17.69	17.66	17.64	17.79	17.77	17.56	17.69	18.27
Sulphur ..	0.49	0.38	0.39	0.27	....	0.44	0.39	1.42
Oxygen...	24.34	24.15	24.39	24.11	....	24.51	24.28	23.93
	<hr/> 100.00	<hr/> 100.00	<hr/> 100.00	<hr/> 100.00		<hr/> 100.00	<hr/> 100.00	<hr/> 100.00

A comparison of the reactions of 41 with those of 37 showed that much less difference existed between the extreme fractions from the blue lupin than between those from the yellow. A ten per cent. solution of 37 in ten per cent. brine gave a considerable precipitate when diluted with twice its volume of water, while three times its volume were required to produce a slight precipitate in similar solutions of 41. Solutions of both were precipitated with equal quantities of acid, 41 not needing the large excess of acid to cause precipitation which the soluble product from the yellow lupin required.

A solution of five per cent. of 37, in ten per cent. brine, even after prolonged heating at 99°–100°, appeared wholly unaffected until the solution was subsequently cooled, when it solidified. A similar solution of 41 began to yield a flocculent coagulum at 75°, which at 80° was voluminous. After heating in a boiling water-bath for some time nearly all the proteid was coagulated. As to the relations of these two substances, what was said on page 474, in our opinion, applies equally in this case.

#### CONCLUSION.

Both yellow and blue lupin seeds contain very little proteid matter soluble in water. The total quantity of proteid soluble in pure water obtained from the yellow lupin amounted to only 0.37 per cent. Of this a part consists of proteose. Whether the remainder is albumin, or a globulin soluble in extremely dilute salt solutions, which therefore could not be completely separated by dialysis, was not determined. Peptone is not contained in the freshly ground seed but is formed in small quantity after prolonged contact with water.



The greater part of the proteid matter contained in these seeds is soluble in saline solutions, the yellow lupin yielding 26.2 per cent. This is the body known as conglutin, but as heretofore described and as usually obtained it is contaminated with other substances present in the seed. Preparations from the blue lupin are usually much purer than those from the yellow, for the latter contain a considerable quantity of some sulphur-containing substance from which conglutin can be separated by fractional precipitation out of dilute salt solutions. This explains why Ritthausen's conglutin from the yellow lupin contained twice as much sulphur as that from the blue lupin.

When purified no difference in properties and reactions can be detected between preparations from the two seeds.

The composition of conglutin, as obtained by us, is shown by the following figures :

## CONGLUTIN.

	Yellow lupin.	Blue lupin.
Carbon .....	50.91	51.13
Hydrogen .....	6.88	6.86
Nitrogen .....	17.93	18.11
Sulphur .....	0.52	0.32
Oxygen .....	23.76	23.58
	<hr/> 100.00	<hr/> 100.00

Conglutin is readily soluble in sodium chloride solutions containing upwards of five per cent. of the salt. By sufficient dilution it is precipitated, a syrupy liquid separating which is rendered opaque and solid by treatment with water. Dissolved in salt solution, it is apparently unaffected by prolonged heating in a boiling water-bath, but solutions thus heated on standing and cooling form a solid opalescent jelly which becomes clear and fluid on again heating. Unlike other globulins conglutin does not yield insoluble (coagulated) products by washing with alcohol or drying.

After exhausting lupin meal with salt solution, a small quantity of proteid can be extracted by two-tenths per cent. potash water, from which it is precipitated by adding acetic acid in slight excess but not by making the solution neutral to litmus. Only one preparation of this substance was made, which gave the following results on analysis :

Carbon .....	51.40
Hydrogen .....	6.79
Nitrogen .....	16.43
Sulphur .....	1.03
Oxygen .....	24.35
	<hr/>
	100.00

Owing to the insolubility of this substance in any but alkaline fluids and the difficulty of making preparations of known purity, nothing further was learned respecting it.

### EFFECT OF MINUTE QUANTITIES OF ACID ON THE SOLUBILITY OF GLOBULIN IN SALT SOLUTIONS.<sup>1</sup>

BY THOMAS B. OSBORNE AND GEORGE F. CAMPBELL.

Received April 12, 1897.

IN a paper on crystallized vegetable proteids by one of us<sup>2</sup> it is shown that the principal globulin of the seed of the castor bean is partly insoluble in a saturated solution of sodium chloride, and partly soluble therein, and that these two parts are alike in composition and but slightly different in reactions. Having found a proteid of similar composition and properties in the sunflower seed, we have again turned our attention to the globulin of the castor bean, with the hope that we might discover the cause of this partial precipitation by saturating its solutions with salt.

A considerable quantity of this globulin was prepared by extracting castor pomace with three per cent. brine at 60° and allowing the filtered extract to cool to the temperature of the room. The proteid thus separated was washed with water and alcohol, and dried over sulphuric acid. It formed a slightly colored dense powder consisting of a mixture of spheroids and octahedral crystals.

Seventy-five grams of this preparation were treated with 750 cc. of ten per cent. salt solution, and after agitating for some time, filtered from a large insoluble residue. This latter was washed thoroughly with ten per cent. brine and the filtrate and washings were united. In this way the substance was separated into two parts, one soluble and one insoluble, in cold salt solution. This solution was then saturated with sodium chloride

<sup>1</sup> From the Report of the Connecticut Agricultural Experiment Station for 1896.

<sup>2</sup> Osborne: *Am. Chem. J.*, 14, 671.

and the large precipitate produced was filtered off, dissolved in 10 per cent. brine and this process twice repeated. The saturated sodium chloride solutions filtered from these precipitations were united and dialyzed free from salt; the proteid thus precipitated was washed with water and alcohol, and dried over sulphuric acid. Thus 12.39 grams of preparation A were obtained, representing the fraction of this globulin soluble in cold ten per cent. brine and *not* precipitated by saturation with sodium chloride. The proteid which had been several times precipitated from solution by saturation with salt, as just described, was dissolved in ten per cent. brine, and the solution filtered perfectly clear and dialyzed. By the usual treatment 18.52 grams of preparation B were obtained, representing the part of this globulin soluble in cold ten per cent. brine, but insoluble in saturated brine.

The part of the globulin which failed to dissolve in cold ten per cent. sodium chloride solution was next treated with salt solution of this strength, heated to 60° and allowed to cool to 14°. The greater part of the proteid was dissolved by this treatment, and after decanting the solution the undissolved residue was treated three successive times in the same way. The solutions obtained by this process were filtered clear from a slight quantity of suspended matters and saturated with sodium chloride, which precipitated all but an insignificant quantity of the dissolved proteid.

This precipitate was dissolved in ten per cent. brine, filtered clear and dialyzed. The precipitated globulin, after filtering off, washing, and drying, weighed 12.37 grams, and formed preparation C.

The part of the original globulin which failed to remain in solution after the above treatment with hot salt solution was dissolved in brine at 60°, filtered clear, and allowed to cool over night. Very nearly all the proteid precipitated on cooling, and was washed and dried, giving preparation D, weighing 1.66 grams.

These four preparations were analyzed with very great care with the following results :

	A.	B.	C.	D.
Carbon.....	50.99	51.10	51.12	51.25
Hydrogen.....	6.92	6.87	6.95	6.97
Nitrogen.....	18.95	18.67	18.83	18.74
Sulphur } .....	23.14	23.36	23.10	23.04
Oxygen } .....				
	100.00	100.00	100.00	100.00
Ash .....	0.19	0.14	0.14	0.41

The difference between these results barely exceed the usual errors of analysis, although several determinations of each element in the different fractions indicate that these differences are not due to analytical errors. It would not be safe, however, to take such slight variations into account, especially when we consider the great difficulty in making perfectly pure preparations of proteids as well as exact combustions. We must, therefore, conclude that no difference in composition is proved to exist between these four preparations which present such marked differences in solubility. A comparative examination of these substances was made with the following results :

In ten per cent. brine at 20°, A dissolved completely, B with the exception of a small residue, C partly, much being insoluble, while D did not dissolve at all. B and C dissolved nearly completely when warmed to 45°.

Five grams of each of A, B, and C were dissolved in 50 cc. of ten per cent. sodium chloride solution by heating to 50°. On cooling to 20°, B and C deposited a very slight amount of proteid, but on cooling to 12°, A gave a clear solution, while B deposited a not inconsiderable quantity of substance and C decidedly more. To five cc. of each of these solutions at 20° were added five cc. of water. A remained clear, B gave a slight precipitate, and from C practically all the dissolved globulin was thrown down, since further dilution of the solution filtered from this precipitate gave only a turbidity. With five cc. more water added to A a turbidity resulted, while the same amount added to B gave a heavy precipitate. The dilution of A and B was continued until the strength of the salt solution was 1.66 per cent., when B yielded no more by further dilution, and A still contained dissolved globulin.

Five per cent. solutions of each of these proteids, in ten per cent. brine, when heated became turbid. A and B at 88°, C at

87°, and flocculent coagula formed in A and C at 90° and in B at 91°, thus showing no difference in relation to heat.

Saturation with sodium chloride of the ten per cent. solution of this globulin gave a small precipitate in A, but completely precipitated B and C.

This partial precipitation of A shows that the substance precipitated by saturating with salt is a derivative of the body originally soluble in saturated brine.

In order to find the effect of minute quantities of acid added to these several fractions, two grams of each were treated with 20 cc. of 0.05 per cent. acetic acid, or five milligrams of acid for each gram of proteid, which caused no noticeable solution. Two grams of salt were added to each whereby A was largely, B partly, and C but slightly dissolved. Heated to 50°, A gave a clear solution, B a nearly clear solution, while C dissolved only partly and precipitated on cooling to 20°.

The acid added to these solutions could not be detected by very delicate litmus paper, the reaction being perfectly neutral.

A solution of A was prepared in exactly the same manner, omitting the acetic acid, and the two solutions compared.

Diluted with an equal volume of water, no precipitate formed in either solution, but with two volumes an abundant precipitate fell in that containing the acid, while only a very slight precipitate formed in the other. Saturated with sodium chloride, the solution with acid gave a large precipitate, that without acid only a small one.

It is thus clear that a quantity of acid too small to be detected with litmus or by analysis causes changes in the fractions soluble in saturated salt solution, whereby products result having the same general properties as those exhibited by the fractions B and C.

In order to obtain more evidence on this point, these experiments were repeated and extended, using crystallized edestin from hemp seed.

Five grams of edestin were suspended in 50 cc. of 0.05 per cent. acetic acid, five grams of salt were added, and the solution was warmed to 50° to dissolve the insoluble "albuminate" present.

Another solution was then prepared in exactly the same man-

ner without using acetic acid. Both solutions reacted perfectly neutral to litmus paper.

Equal volumes at the same temperature, and in test-tubes of the same size were immersed in the same bath of cold water. The solution containing acid precipitated first and in far greater amount than the other.

Five cc. of each were diluted with an equal volume of water at 20°. The solution with acid gave a much greater precipitate than the other. After allowing these to stand and cool to 10°, the precipitates were filtered off and one drop of strong acetic acid was added to each filtrate. The solution which had been made with acid gave only a turbidity, while a considerable precipitate formed in the other, showing that dilution precipitates the solution to which the acid had been added far more readily than the solution without the acid.

Equal volumes of these solutions were saturated with salt, the precipitates filtered off, and one drop of acetic acid was added to each filtrate. That from the solution made with acid gave only a turbidity, while the other gave a very heavy precipitate.

Here again we see that the addition of a quantity of acid, too small to detect after the solution has been made, brings about changes similar to those naturally occurring in the seeds and extracts of the castor bean and sunflower and to those following the addition of acid to that part of the globulin of the castor bean which is soluble in saturated salt solutions.

Whether such changes occur only through the influence of acids is a question not settled, and regarding which some doubt is raised by the fact that preparations of crystallized edestin which were originally soluble in ten per cent. sodium chloride solution with the exception of a small quantity of "albuminate" and yielded solutions which gave only traces of precipitates on saturating with sodium chloride, were found, after keeping dry and in cork-stoppered bottles two and four years, to have become largely insoluble in cold salt solution and to yield solutions which were nearly completely precipitated by saturating with salt. The insoluble portion dissolved nearly completely in ten per cent. brine at 60° to a solution precipitated somewhat by cooling to 20°, and abundantly at lower temperatures, copiously precipitated by dilution with an equal volume of water, and

almost completely precipitated by saturating with sodium chloride. It is not at all impossible that this change, too, may have been caused by acid, for these preparations stood for several years in the laboratory, the air of which at times contained some acid vapors. We thus see the same change taking place in the dry proteid on long keeping as those definitely caused by minute quantities of acid.

That this change to a condition in which the globulin is precipitated by salt is an intermediate step towards the formation of the insoluble form, the so-called "albuminate" of Weyl is evident from what has already been stated, especially the fact that by treatment with warm salt solution this insoluble matter can be changed into the form soluble in cold salt solution and precipitable by saturation with salt.

In this connection it is interesting to note that the only animal globulin obtained from an acid tissue is myosin, and that this myosin not only is readily precipitated by saturating with salt, but quickly and spontaneously changes to the insoluble form known as syntonin. In the dead muscle the amount of acid greatly exceeds that used in our experiments, for its presence is plainly shown by the strong acid reaction of the muscle serum. In alkaline muscle plasma myosin is not found, but myosinogen, paramyosinogen, and myoglobulin. The last three are described as precipitated by saturation with sodium chloride, but it may be that when tested in this respect the formation of acid had already begun and had reached a point where it caused precipitation with salt, but could not be detected by the usual tests.

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## THE PROTEIDS OF THE SUNFLOWER SEED.<sup>1</sup>

BY THOMAS B. OSBORNE AND GEORGE F. CAMPBELL.

Received April 12, 1897.

THE only published observations on the proteid of the sunflower seed which we have found were made by Ritthausen<sup>2</sup> and by Vines.<sup>3</sup> By extracting with very dilute alkali Ritthausen obtained from finely ground oil-free meal 44.71 per cent. of proteid, having the composition given under 1. By treating with sodium chloride brine, diluting the extract with

<sup>1</sup> From the Report of the Connecticut Agricultural Experiment Station for 1896.

<sup>2</sup> Pflüger's Archiv., 21, 89, 1880.

<sup>3</sup> *J. Physiol.*, 3, 93.

five volumes of water and passing carbon dioxide through the solution he got 25.3 per cent. with the composition given under 2, and by exhausting a preparation obtained in the same manner as 1 with brine, and proceeding as with 2, he got a preparation whose analysis is given under 3.

SUNFLOWER PROTEID. RITTHAUSEN.

	1.	2.	3.
Carbon .....	51.88	51.51	51.18
Hydrogen.....	6.66	6.76	6.82
Nitrogen.....	17.99	18.21	18.06
Sulphur .....	0.71	0.61	
Oxygen .....	22.76	22.91	23.94
	<hr/> 100.00	<hr/> 100.00	<hr/> 100.00

Vines states that if a section of sunflower seed be treated with ether to remove oil it will be found that the aleurone grains, though readily soluble in ten per cent. sodium chloride solution, will not dissolve in saturated solution; if, however, they be treated with alcohol instead of ether, the globulin of which these grains consist behaves like vitellin, that is, it dissolves in a saturated solution of sodium chloride.

Vines further states that "it is of interest to note the fact that most of the substances which I found in the grain recur in the crystalloids, more especially vitellin and its derivatives; thus the peculiar globulin which forms the crystalloids of *Ricinus* appears to be in the grains of *Helianthus*."

Ritthausen's results indicate that by far the greater part of the proteid matter of the sunflower seed has a uniform composition, and that a large part of this proteid is insoluble in salt solution, but soluble in dilute alkali. The composition which he found for this proteid resembles that of the globulin edestin, which we have found in many seeds, the only difference being a slightly lower content of nitrogen. On this account it seemed to us desirable to examine this proteid and determine its relation to edestin. This was the more important, because Vines' statement of its behavior when treated with ether and with alcohol showed it to possess the same peculiar relations to salt solutions observed by one of us<sup>1</sup> in studying the globulin of the castor bean, *Ricinus communis*. As the deportment of globulins to saturated sodium chloride solutions has been made the basis of

<sup>1</sup> Osborne: Report Conn. Expt. Station, 1892, p. 138, and *Am. Chem. J.*, 14, 671.



a division of these bodies into two main classes, it is important for us to know whether this is founded on fundamental differences in the proteids, or is simply due to the unlike conditions under which the proteids are found.

Sunflower seeds were crushed and a large part of the woody shells removed. The meal was then ground under benzine and after freeing from oil, air-dried. This meal when treated with ten per cent. sodium chloride brine yielded an extract of a strong blackish green color, from which a considerable quantity of proteid could be separated by dilution, by dialysis, or by saturation with sodium chloride.

When heated, this extract becomes turbid at 48° and flocks separated at 62°. The solution heated to 75° and filtered from this slight coagulum yielded a large precipitate when saturated with salt, thus showing that most of the substance thus precipitated is not, as *myosin* is said to be, coagulated below 75°.

The unheated extract saturated with sodium chloride gives a precipitate which when dissolved in ten per cent. brine coagulates at the same temperature as the original extract, but the amount of this coagulum is but a small fraction of the substance precipitated by saturation with salt.

The following preparations were made, but as subsequently pointed out, were found to be more or less impure, so that these results have value only as affording evidence of the uniform composition of the globulin extracted by salt solution from the sunflower seed.

	1	2	3	4	5
Carbon .....	51.57	51.77	51.65	51.69	51.85
Hydrogen .....	6.81	6.83	6.72	6.80	6.84
Nitrogen .....	18.16	18.20	18.17	18.24	18.00
Sulphur } .....	23.46	23.20	23.46	0.78	23.21
Oxygen } .....				21.49	
	100.00	100.00	100.00	100.00	100.00
		6	7	8	9
Nitrogen .....		18.20	18.23	18.09	18.07

Of these, 1 is the total globulin extracted by brine from one portion of oil-free meal; 2, 3, 4, and 5 are fractional precipitates from another similar extraction; 6, substance precipitated by saturating the salt extract with sodium chloride; 7 and 8, substance soluble in saturated sodium chloride solution; and 9, that

precipitated by cooling an extract made with a one and a half per cent. salt solution heated to 60°.

These results show that the most abundant proteid of the sunflower seed consists of a single globulin, and that the proteid precipitated by saturating with sodium chloride contains the same amount of nitrogen as the proteid soluble in a saturated solution of this salt. As Vines stated that the substance of the aleurone grains was soluble in a saturated salt solution after treatment with alcohol, while after treatment with ether it was insoluble therein, although soluble in ten per cent. salt solution, we thought that possibly by treating our meal with alcohol we might remove some substance, perhaps an acid soluble in alcohol, but insoluble in ether, which might be the cause of this peculiar behavior of the proteid. We accordingly extracted a quantity of sunflower meal with alcohol of 0.820 sp. gr., and in order to determine whether acid had been removed we attempted to titrate a portion of the extract with a one per cent. solution of potash. On adding the alkali a colored precipitate resulted, which rendered the indicator (*phenolphthalein*) useless. The attempt was then repeated, omitting the indicator. When the potash solution was added a bright chrome yellow color resulted which gradually increased with the formation of a precipitate as the quantity of the potash was increased. With a larger excess of potash the precipitate redissolved. This reaction we found to be due to helianthotannic acid.<sup>1</sup> The results of our investigation of this acid will be given in another paper.

Having now found a very delicate test for this acid, we applied it to our preparations of globulin and obtained a strong reaction in every case. It was therefore necessary to remove this acid from the meal before attempting to obtain the proteid and accordingly the extraction of the meal with alcohol was continued. It was, however, practically impossible to remove the acid so completely as to obtain no yellow reaction when the extract was treated with potash.

The meal which had been nearly freed from this acid was washed with ether and air-dried. 100 grams were extracted with ten per cent. sodium chloride brine and the filtered extract saturated with salt. An abundant precipitate separated, just as

<sup>1</sup> Ludwig and Kromayer, N. Br., 99, 1, 285.

with meal which had not been treated with alcohol. This was filtered off, dissolved in ten per cent. brine and again precipitated by saturation with salt. This precipitate was again dissolved in salt solution, filtered perfectly clear, and dialyzed. The globulin which was thus precipitated was filtered out, washed with water and alcohol and dried over sulphuric acid. This preparation, 10, weighed seven and four-tenths grams and had the following composition :

SUNFLOWER GLOBULIN, PREPARATION 10.

Carbon .....	51.27
Hydrogen .....	6.55
Nitrogen .....	18.21
Sulphur.....	0.78
Oxygen .....	23.25
	<hr/>
	100.00
Ash .....	0.31

The saturated sodium chloride solutions filtered from the two precipitations of 10, were united and dialyzed until free from chloride; the resulting precipitate was filtered out and treated as 10 had been. Preparation 12 was thus obtained, which on analysis gave the following results :

SUNFLOWER GLOBULIN, PREPARATION 12.

Carbon .....	51.58
Hydrogen .....	6.55
Nitrogen .....	18.29
Sulphur.....	0.97
Oxygen .....	22.61
	<hr/>
	100.00
Ash .....	0.29

As both the preceding preparations were found to contain detectable quantities of helianthotannic acid another attempt was made to prepare some meal which should be practically free from this acid.

One hundred grams of meal were therefore extracted in a Squibb's percolator with alcohol of 0.820 sp. gr., the whole being kept at 65° C. until 1500 cc. of extract were obtained.

The temperature was then raised to 75° and the extraction continued, about seven liters of alcohol being passed through the

meal. The last two liters were evaporated and left a residue weighing only 0.28 gram.

The meal residue was air-dried and extracted with ten per cent. sodium chloride solution. The extract was then filtered clear and saturated with ammonium sulphate, the precipitated proteid filtered out, dissolved in brine, the solution filtered perfectly clear and dialyzed.

The proteid was thus precipitated in large spheroids and was filtered out, washed with water and alcohol, dried over sulphuric acid and found to weigh 15.5 grams, preparation 13. This substance was freer from coloring matter than any before made, and had the following composition :

SUNFLOWER GLOBULIN, PREPARATION 13.

Carbon .....	51.34
Hydrogen .....	6.99
Nitrogen .....	18.58
Sulphur.....	1.00
Oxygen .....	21.71
	<hr/>
	100.00
Ash .....	0.47

This preparation, which was very nearly white in color after drying, dissolved almost wholly in ten per cent. sodium chloride brine at 20°, giving a solution slightly tinged with greenish brown, which on dilution yielded an abundant precipitate that on warming, while suspended in the diluted solution, redissolved completely and again separated on cooling in spheroids, and on settling united with a coherent layer.

Solutions in ten per cent. sodium chloride brine behaved as follows :

When saturated with magnesium sulphate at 20° or sodium sulphate at 34°, the proteid was completely thrown out of the solution. When saturated with sodium chloride it was partly precipitated.

With mercuric chloride, picric acid, or tannic acid a heavy precipitate was produced.

With minute quantities of nitric, sulphuric, hydrochloric, or acetic acid the globulin was precipitated.

In pure water this preparation formed a plastic mass, but none dissolved.

In the water containing a minute quantity of acid it dissolved readily and completely.

With the xanthoproteic, Millon's, biuret and Adamkiewics' tests the usual preteid reactions were obtained.

When dissolved in ten per cent. sodium chloride solution and tested for heat coagulation point in the usual manner a turbidity formed at  $90^{\circ}$ , and a flocculent coagulum began to separate at  $93^{\circ}$ , increasing as the temperature was raised toward  $100^{\circ}$ . After heating sometime in a boiling water bath a considerable coagulum formed, yet a large proportion of the substance still remained in solution, as shown by the voluminous precipitate produced on adding acetic acid to the solution filtered from the coagulum.

In composition and reaction this preparation agrees with the globulin edestin, except that a part is precipitated by saturating its solutions in brine with sodium chloride. In composition the part precipitated by saturating with salt and that remaining in solution are alike. We have in another paper<sup>1</sup> pointed out that the globulin of the castor bean shows a similar behavior, and that the part precipitated by saturating with salt is a derivative of the part soluble in saturated salt solutions. We have further shown that the addition to a solution of edestin of a quantity of acetic acid too small to detect after mixing with the proteid, causes a precipitation of the edestin on saturating its solution with brine, and that under these conditions, the proteid otherwise behaves like the globulin from the castor bean and sunflower seed.

As helianthotannic acid contains about fifty-three per cent. of carbon, the presence of two per cent. of this acid in our preparation would but slightly raise the figures obtained for carbon and reduce those for nitrogen by about 0.35 per cent. The composition of the purer preparations which we have obtained differ from edestin to about this extent.

It is therefore our opinion that the sunflower seed contains as its principal proteid the globulin edestin, but that as obtained by extraction from the seed, this is mixed with helianthotannic acid, from which we have not succeeded in separating it completely.

Having thus found that a large part of this globulin is insolu-

<sup>1</sup> This Journal, 19, 482.

ble in saturated salt solutions under all the conditions of our tests, we were led to repeat Vines's experiments, but have been unable to confirm his observations, the aleurone grains appearing to be wholly unaffected by saturated salt solution after treatment of the seed with alcohol.

## THE PROTEIDS OF THE COW PEA.<sup>1</sup>

(*Vigna Catjang.*)

BY THOMAS B. OSBORNE AND GEORGE F. CAMPBELL.

Received April 12, 1897.

THE proteids of this plant have never been, to our knowledge, the subject of study. Because of its great and increasing agricultural importance, and as a plant differing botanically from those included in our investigation of "legumin," the proteids of its seeds have much interest. The material examined was prepared by coarsely grinding the peas, separating the black seedcoats by a current of air, and then grinding the coarse meal to a fine flour. Two kilograms of this flour were treated with a quantity of ten per cent. sodium chloride solution, the extract was strained through fine bolting-cloth and allowed for three hours to deposit the greater part of the suspended starch. The extract was then run through a DeLaval centrifugal separator, whereby most of the remaining suspended starch and fiber was removed, and lastly was filtered perfectly clear by passing through a thick layer of filter paper pulp. The extract was saturated with ammonium sulphate, the precipitated proteids collected on a filter and dissolved in brine. The solution was filtered perfectly clear and dialyzed for four days.

The proteid, thus separated in the form of spheroids, was designated *A*, and the solution filtered therefrom was marked *B*. *A* was collected on several paper filters. One portion was washed very thoroughly with water and with alcohol and, dried over sulphuric acid, gave preparation 1, which weighed 29.7 grams. The rest of *A* was dissolved in one liter of five per cent. sodium chloride brine, and the solution filtered perfectly clear. On adding one liter of distilled water a large precipitate, *D*, separated, which was allowed to settle over night. The liquid, *C*,

<sup>1</sup> From the Report of the Connecticut Agricultural Experiment Station for 1896.

was then decanted from the proteid, *D*, which had formed a coherent deposit. *D* was dissolved in 150 cc. of ten per cent. sodium chloride brine, with which it readily yielded a clear solution, and water was added to make the volume one liter. A rapidly settling precipitate appeared that soon united to a coherent layer, from which the nearly clear liquid was decanted. After thoroughly washing this precipitate with water and with alcohol and drying it over sulphuric acid, there resulted 50.9 grams of preparation 2. The solution decanted from 2 was treated with 200 cc. of water, causing a precipitate which, washed and dried as before, gave 12.83 grams of preparation 3. Similarly the solution decanted from 3, when mixed with 200 cc. more water, gave six and two-tenths grams of preparation 4.

The solution decanted from 4 was dialyzed until chlorides were removed, which treatment precipitated all but a trace of the dissolved proteids. In this way four and four-tenths grams of preparation 5 were obtained.

The solution *C*, decanted from the precipitate *D*, as described on page 494, was diluted with 500 cc. of water. The proteid thus thrown down, after washing and drying, formed preparation 6, which weighed 16.9 grams. The filtrate from 6 was dialyzed for two days, and a deposit obtained weighing, when dry, 10.5 grams, 7. The filtrate from 7 was nearly free from proteid matter.

These preparations were analyzed, after drying at 110°, with the following results :

	1.	2.	3.	4.	5.	6.	7.
Carbon.....	52.45	52.69	52.63	52.56	52.52	52.59	52.27
Hydrogen....	6.92	6.77	6.90	6.98	7.04	7.08	6.97
Nitrogen....	17.16	17.18	17.50	17.18	17.27	17.24	16.69
Sulphur.....	0.40	0.57	0.52	0.62	0.53	0.56	0.50
Oxygen .....	23.07	22.77	22.45	22.66	22.64	22.53	23.57
	<hr/>	<hr/>	<hr/>	<hr/>	<hr/>	<hr/>	<hr/>
	100.00	100.00	100.00	100.00	100.00	100.00	100.00
Ash.....	0.32	0.64	0.47	0.50	0.42	0.45	0.16

It will be noticed that the first six preparations are nearly identical in composition. Of these, 1 represents the globulin precipitated by dialyzing the solution of the ammonium sulphate precipitate (which contained all the proteid matter extracted from the seed). 2, 3, 4, and 5 are four fractions of that portion of the substance (of which 1 is a part) that is most readily precipitated by dilution. 6, which also agrees with the foregoing,

is that part of the remainder thrown down by further dilution, the solution filtered from the precipitate, yielding 2, 3, 4 and 5. In composition, 7 differs from 1-6. Although the figures obtained for 1 closely agree with those for 2, 3, 4, and 5, the former has been shown to contain about ten per cent. of the globulin, 7, whose presence in this proportion affects but slightly the percentage composition of 1.

Remarking that 7 agrees in composition with the globulin phaseolin and that preparations 1-6 have a composition corresponding to a mixture of equal parts of phaseolin and legumin, we thought it important to determine whether or not this substance contained these two proteids. Phaseolin being much more readily soluble in dilute saline solutions than legumin, these globulins may be separated by fractional precipitation. Accordingly, twenty grams of 2 were treated with 500 cc. of five per cent. sodium chloride brine, and the solution was filtered off from the undissolved "albuminate." The filtrate, which measured 378 cc., was diluted with four times its volume of water, to produce a one per cent. brine, in which phaseolin dissolves freely and legumin somewhat sparingly. An abundant precipitate fell which was filtered out, washed, and dried, as usual, and formed preparation 8. The filtrate from 8 was saturated with ammonium sulphate, and the very small precipitate produced was dissolved in water and dialyzed. Only three-tenths gram of globulin was thus obtained, showing that very little of the proteid was soluble in one per cent. salt solution.

The residue which remained undissolved after treating 2 with five per cent. sodium chloride brine, was washed by decantation with salt solution, heated to about 50°, and the filtered washings dialyzed. Preparation 9 was thus precipitated.

The portion of 2 that remained undissolved by this treatment was thoroughly washed with water and alcohol and dried over sulphuric acid, making preparation 10. These were dried at 110° and analyzed with results that follow :

	8.	9.	10.
Carbon.....	52.74	52.70	52.87
Hydrogen.....	6.94	6.97	6.95
Nitrogen.....	17.22	17.21	17.29
Sulphur.....	0.40	0.42	0.49
Oxygen.....	22.70	22.70	22.40
	<hr/>	<hr/>	<hr/>
	100.00	100.00	100.00
Ash.....	0.66	0.73	0.64



It is evident that no fractional separation was accomplished by this treatment, and that the most abundant globulin of the cow pea must be regarded as a distinct proteid, differing from any heretofore described. For this proteid we propose the name *vignin*.

Its composition as represented by an average of the foregoing figures is here stated.

VIGNIN.	
Carbon.....	52.64
Hydrogen .....	6.95
Nitrogen .....	17.25
Sulphur.....	0.50
Oxygen .....	22.66
	<hr/>
	100.00

The reactions of vignin are as follows: In cold or warm water, when free from soluble salts, it dissolves to a considerable extent, the solutions resulting being precipitated by adding a very little salt. The precipitate so separated dissolves completely on adding more salt.

It is readily soluble in sodium chloride solutions, containing upwards of five per cent. of salt, from which solutions it is promptly precipitated by dilution. In two and one-half per cent. salt solutions relatively little, and in one per cent. very little, dissolves. It is readily and completely soluble in dilute acids and alkalies in absence of salts. Solutions in very dilute nitric or hydrochloric acid are precipitated by salt or by an excess of these acids. In dilute sulphuric acid it is much less readily soluble than in the acids just named, and is not precipitated by an excess of sulphuric acid and but slightly on adding salt. Solutions in very dilute acetic acid are not precipitated by an excess of this acid but give heavy precipitates on adding sodium chloride. Dissolved in one-half per cent. sodium carbonate solution, the proteid is precipitated by neutralization. The separated proteid at once dissolved on adding salt. Dissolved in ten per cent. sodium chloride brine, this globulin behaves as follows :

By hydrochloric acid it is not precipitated until a relatively considerable quantity of the acid is added. By this acid the globulin is less readily thrown down than legumin but more readily than phaseolin.

The same is true of acetic acid, of which a somewhat large quantity is required to cause a precipitate. Phaseolin is not precipitated at all under these conditions.

By diluting the salt solutions of vignin it is apparently more readily precipitated than legumin, and far more readily than phaseolin.

Saturation of solutions of vignin with sodium chloride or magnesium sulphate gives no precipitate, but saturation with sodium sulphate at 34° causes nearly complete precipitation of the proteid.

Mercuric chloride gives no precipitate, tannic acid and picric acid make heavy precipitates in its solutions.

With Adamkiewics', Millon's, the biuret and xanthoproteic tests the usual proteid reactions are obtained.

Strong solutions of this globulin dissolved in ten per cent. sodium chloride become turbid when heated to 98°, and after continued heating set to a jelly.

Besides vignin the cow pea contains a small quantity of proteid matter represented by preparation 7, which in composition, as well as reactions, agrees very closely with phaseolin. Phaseolin differs from all other plant globulins, which we have thus far observed, in not being precipitated from its solution in ten per cent. sodium chloride brine by a large quantity of acetic acid. In this respect 7 behaves like phaseolin.

The composition of phaseolin as obtained from different seeds is shown by the following statement :

PHASEOLIN.			
	Cow pea.	Kidney bean.	Adzuki bean.
Carbon.....	52.27	52.58	52.56
Hydrogen.....	6.97	6.84	6.97
Nitrogen.....	16.69	16.47	16.45
Sulphur .....	0.50	0.56	0.57
Oxygen .....	23.57	23.55	23.45
	<hr/> 100.00	<hr/> 100.00	<hr/> 100.00

The solution *B*, filtered from *A*, as described on page 494, was saturated with ammonium sulphate and the small precipitate produced was dissolved in a little dilute salt solution, filtered perfectly clear, and dialyzed for two weeks. A precipitate resulted which was filtered out, washed with water and alcohol,

and dried over sulphuric acid. This preparation, 11, weighed three and two-tenths grams. The filtrate from 11 was dialyzed ten days longer, but as nothing separated the solution was dialyzed against alcohol. A small precipitate, 12, appeared, which weighed 3.75 grams.

These preparations, after drying at 110°, were analyzed with the following results :

	11.	12.
Carbon .....	53.13	53.36
Hydrogen .....	7.09	7.05
Nitrogen .....	16.51	16.21
Sulphur .....	1.09	1.13
Oxygen.....	22.18	22.25
	<hr/>	<hr/>
	100.00	100.00
Ash .....	0.65	0.81

It will be noticed that these two preparations agree quite closely in composition. Although 11 was precipitated by dialysis in water and is unquestionably a globulin, while 12 could not be precipitated by even prolonged dialysis, nevertheless it is our opinion that these are one and the same proteid. In a subsequent paper we hope to point out the relations of this globulin to the proteids obtained similarly from other leguminous seeds.

CONCLUSION.

1. The chief proteid of the cow pea is a globulin, much resembling the legumin of the pea and vetch, but essentially different in composition and properties, for which we propose the name *vignin*. Its composition, as found by the average of closely agreeing analyses of nine fractional precipitates, is as follows :

VIGNIN.

Carbon.....	52.64
Hydrogen .....	6.95
Nitrogen .....	17.25
Sulphur.....	0.50
Oxygen .....	22.66
	<hr/>
	100.00

2. Besides vignin, the cow pea contains a globulin which has the composition and, so far as could be determined, the properties of phaseolin, which we have found in the kidney bean

(*Phaseolus vulgaris*), and the adzuki bean (*Phaseolus radiatus*).

3. The cow pea contains a third globulin, extremely soluble in very dilute salt solutions, which could be precipitated but partially by dialysis in water and completely only in the coagulated form by dialysis in alcohol. This substance closely resembles, in properties and composition, bodies obtained from several other leguminous seeds. Its composition, as found by analysis of two precipitates, one obtained by dialysis in water and the other by further dialysis in alcohol, is as follows :

Carbon.....	53.25
Hydrogen .....	7.07
Nitrogen .....	16.36
Sulphur.....	1.11
Oxygen .....	22.21
	<hr/>
	100.00

## ON THE MANUFACTURE OF DYNAMITE.

BY G. E. BARTON.

Received April 22, 1897.

UNDER the general term dynamite are included two classes of mixtures. The first of these consists of nitroglycerol, held by an absorbing medium, such as woodpulp or kieselguhr, together with various other bodies used as fillers, the principal one being sodium nitrate; this latter body also adds to the strength of the dynamite when woodpulp is the absorbent used by furnishing oxygen for the combustion. The second class, more properly called gelatin dynamites, consists of nitroglycerol gelatinized by means of nitrated cellulose, much the same substances being present as fillers, but considerable less absorbing material in proportion to the amount of nitroglycerol. It is to the former class of mixtures that this paper relates, although most of it is equally applicable to the latter. Most of the dynamite used in this country is of the first class, as it is less costly and equally serviceable, except in wet holes.

The choosing of a site for a dynamite factory is a matter into which many factors enter. It is much more convenient, cheaper, and safer to have the part of the plant used in making the nitroglycerol on a hillside, as it is then possible to allow that liquid to flow from building to building in pipe lines. Authorities usually hold that the soil should not be sandy on account of the

danger from sand blowing into the buildings and finally giving rise to friction in some part of the apparatus. The danger from this source is very small, as can be seen from the fact that one factory (the only one known to the author on such soil) has been located for about fifteen years on a sandy hillside without having an accident which could be traced to this cause. The only precautions taken are to carefully clean everything after each day's work, which must be done anyway, and the sweeping out of the sand occasionally as it accumulates before the doors. The sandy soil probably plays a very important part in another direction, for though the most violent thunder storms sweep over the region during many months of the year, there has never been a building struck by lightning. No lightning protectors whatever are used. The explanation of this fact seems to be that the light buildings, with their very light foundations, are much poorer conductors of electricity than the surrounding trees, the roots of which extend into the moist earth below. Another advantage is that the shock of the most violent explosion is not conducted to great distances, as is the case in other soils. In the factory before mentioned a catch box for the nitroglycerol, carried away in the wash waters, in which about one hundred and fifty pounds of that explosive had accumulated (contrary to orders) exploded. It was situated not more than one hundred feet from the storehouse, in which was considerable nitroglycerol at the time, but this did not explode, although the flying *débris* damaged the building badly.

The manufacture of nitroglycerol is the most important point to be considered in connection with the manufacture of dynamite and the different parts of the process will be taken up in the order in which they occur. The nitration is best conducted in a nitrator of cylindrical shape and made of lead with a bottom sloping slightly toward the point at which the faucet for drawing off the mixture of nitroglycerol and acids is placed. The top is made of lead and has several panes of glass set in it, through which the workman watches the operation. From the center a ventilator of lead passes up through the roof. Two thermometers are fixed, one with the bulb near the surface of the liquid, and the other with it in the lower strata. These are in front of the operator at work, and guide him. The glycerol valve is

controlled with the left hand, and the compressed air for agitating with the right.

The method of mixing by compressed air is beyond doubt the safest, as it gives a more thorough mixing, allows more than one cooling coil to be used, and is less liable to get out of order. A drawback, common to all mechanical agitators, is the unreliability of any piece of machinery exposed to the acid fumes which are always present in and near the nitrating house. The air after leaving the compressor should be passed through an iron drum containing sulphuric acid, and arranged in the same manner as the ordinary bottle for washing gases in the laboratory, in order that any moisture it may contain may be removed.

Everything being in order and tested as far as possible, the operator sets the lead trough, which connects the discharging faucet with the separator, or drowning tank, as desired, to connect with the drowning tank, starts the water running into the tank so as to give some circulation and consequent stirring there in case it becomes necessary to drown the charge and allows the mixed acids to run into the nitrator from a small tank, into which just enough for one charge has previously been forced from the acid store tank outside the danger area by means of a montejus and compressed air. The cooling coils furnish enough water to keep up a circulation in the drowning tank when allowed to discharge into it. About 1,500 pounds of mixed acid is found to be an economical charge, and to this should be added from 210 to 230 pounds of glycerol, according to the conditions. It is economical to increase the glycerol used, even though the percentage yield decreases, as long as a pound of glycerol adds a pound to the yield of nitroglycerol. The acids used should have the following composition: Sulphuric acid, 61.9 per cent.; nitric acid, 34.5 per cent.; oxides of nitrogen, calculated as nitrogen trioxide, 0.7 per cent., with not more than a trace of chlorine and iron. The glycerol must have approximately the following composition, when examined by the method given in this Journal, 17, 277: Ash, trace; carbonaceous residue, 0.012 per cent.; sodium chloride, 0.002 per cent.; total acid equivalent, 0.05347; permanent specific gravity, 1.2653; specific gravity, 1.2634; higher fatty acids, none; reaction, neutral. During the process of nitration the temperature should not

be allowed to go above 88° F. The yield by this method is greater the shorter the time employed in the process, so that in the winter, when a run can be made in one-half an hour or less, fifteen or twenty pounds more of glycerol can be used without decreasing the percentage yield. This is partly due to the fact that the shorter the time the less nitric acid is blown out of the mixture in agitating. No economical method has been devised for recovering the acid thus lost or for reducing the temperature during the summer to the point easily obtainable in this climate during the winter months.

The nitration being finished, the trough is placed so that the mixture can flow into the separating boxes, which transfer ought not to take over three minutes. It is usually held that the separators should be in another building, but many factories in this country have them in the same one with the nitrator. By this method only one drowning tank is required, while if the buildings are far enough apart for one to escape injury from an explosion in the other, two must be provided. It also avoids the trouble which would otherwise be caused by passing the mixture of acids and nitroglycerol through a long trough.

It is almost impossible to avoid some of the mixture remaining in the hollows of the trough, and this in a few hours, especially during the summer, becomes dangerous.

While an explosion would not necessarily be communicated to either building, it must at least injure the line and delay work. No way would be at hand of disposing of the run then in the nitrator, except by drowning, with the consequent loss of the spent acids. The disadvantage is that an explosion destroys more apparatus and material. The danger in a building containing the separators and nitrator is not increased to any extent, as both operations, when properly conducted, give ample warning before an explosion. The building must, of course, be arranged with several exits.

Two men working with two separators and a nitrator, can easily dispose of twelve runs in a working day of ten hours, which means 5,500 pounds of nitroglycerol. If it is necessary to make more, such a plant can be forced to fourteen or fifteen runs a day, under favorable conditions, by working a little overtime. If still more nitroglycerol be required, it is best to build another

similar plant, far enough removed from the first to avoid danger. This latter plan also has the advantage that a single explosion does not entirely stop the production, which is a thing greatly to be desired, as anyone familiar with the demands of trade for the rapid filling of orders will appreciate.

The separators should be cylindrical lead boxes, containing both cooling coils and an arrangement for agitating with air, the latter for use only in emergencies. The bottom is made slightly sloping towards the point where the cock for drawing off both acids and nitroglycerol is placed. The top should be covered with lead, and have glass windows for viewing the fumes given off during the operation. It is necessary to have a narrow pane of glass in the side next to the cock, by means of which the operator is enabled to see when all the acids have been drawn off, and interrupt the flow before any of the nitroglycerol goes into the second separator. The spent acids having been disposed of, a short lead trough is then set so that the nitroglycerol can flow in a thin sheet into a small tank half filled with water, and connected with the wash-house. A stream of water, sufficient to keep the liquid in this tank at a constant level, is turned on at the same time. The nitroglycerol flows from here into the wash-tank in the wash-house, the stream of water being kept up till the nitroglycerol is drowned, and a sufficient quantity of water passed through the pipe line to clean out the last traces.

The wash-tanks should be made of wood, and lined with lead. The agitation is best done with compressed air. Two faucets are set in each of these tanks, one at the bottom for drawing off the nitroglycerol at the end of the washing, and one above the surface of the explosive through which the wash-waters escape. An alkaline wash must always be used at least once, and the nitroglycerol tested with litmus paper before it is allowed to go to the storehouse. The disposal of the wash-waters is a problem which every manager must solve for himself according to conditions at hand, but it will effect quite a saving if they are allowed to flow through a series of compartments in which the little nitroglycerol left in them has a chance to settle out. The nitroglycerol should be removed from these compartments at least once a week. The lead lining to the wash-tanks should be insisted upon, as otherwise the fibers of the wood are opened by



the action of the acid and alkali, and become saturated with nitroglycerol, making the repairing or destruction of the tanks dangerous. The author has traced at least one explosion to this cause.

From the wash-house, the nitroglycerol may be allowed to flow at once into the storage tanks, which are in a separate building. In this country, where there is no limit placed on the amount of nitroglycerol which may be stored, or the length of time it may be kept, no filtering or drying process is necessary. There should be several tanks in the storehouse, and the nitroglycerol should stand twenty-four hours before being mixed with the absorbent, thus giving time for the small amount of moisture which it still contains to become thoroughly separated. Each tank should be tested with litmus paper every day, and if any signs of acidity are developed, the nitroglycerol must at once be destroyed or rewashed. The pipe line from the wash-house should be so arranged that it may be broken when not in actual use, thus preventing the communication of an explosion from one building to the other. It should also be carefully guarded against freezing in winter, and becoming overheated in summer.

The spent acid, which we lost track of as it left the first separators, flows in the usual form of trough to the second separators, where the process is continued for at least three, preferably five days. These separators are best oblong lead boxes, having a capacity sufficient to accommodate the spent acid from three runs, and are furnished with cooling coils and air agitators, the last for use only in emergencies. The top of these boxes should have the shape of three quadrangular pyramids, set side by side. These pyramids terminate in glass cylinders about twelve inches in height and four in diameter, which have a glass plug ground into them about six inches from the bottom. The tops of these cylinders are covered with ground glass plates in order that the air may be excluded from the surface of the liquid as much as possible. The top plates having been removed, the spent acid is allowed to flow into the box until it is filled nearly to the top of the glass cylinders. The nitroglycerol finds its way to the surface of the liquid, and when it has accumulated to the depth of an inch or so, the lower level is brought opposite the plug in the side of the cylinder by drawing out a little of the spent acids,

the plug is removed and the nitroglycerol allowed to flow out and into a lead saucer just below, from which it passes into a dish set to catch it under the spout of the saucer. It must be at once emptied into a pail and carried to the wash-house to be washed, or else drowned in a small tank provided in the separating house. The latter plan is preferable, as the danger of an explosion from the shock of dropping a pail is much less after the nitroglycerol has been thoroughly washed.

How to dispose of the spent acids from the nitroglycerol manufacture, which contain from seventy to seventy-four per cent. of sulphuric acid and from seven to twelve per cent. of nitric acid, is a question which probably has caused managers of dynamite factories more thought than almost any other problem connected with the business. It can hardly be said to be solved satisfactorily yet, but in this country the weight of opinion is in favor of regaining the acid. For this purpose it is run at once from the second separators into a montejus and blown into a tank situated near the top of a Glover tower from which it can be run directly into the tower without further precautions. The nitric acid is condensed in any of the usual ways, while the sulphuric acid runs into a tank at the foot of the tower. The sulphuric acid comes out at  $58^{\circ}$  B, or over, in a well-managed tower, and the nitric acid can be kept above  $36^{\circ}$  all the time, usually near  $38^{\circ}$  B. Care must be taken to arrange the pipe leading from the montejus at the separating house to the tank at the Glover tower, so that it will drain itself thoroughly, as otherwise a sediment, composed mostly of lead sulphate, will settle out, together with any small amount of nitroglycerol the acids may still contain, and finally cause an explosion.

A few general rules to be observed in the manufacture of nitroglycerol may be mentioned here :

Nitroglycerol should never be carried in pails when it is possible to avoid it.

All receptacles which contain the nitroglycerol and acids at the same time should be covered so that neither water nor other foreign substance may accidentally come in contact with them. The writer has seen heating sufficient to necessitate the drowning of the contents of one of the second separators, caused by a small piece of wood falling into the mixture.

All receptacles for nitroglycerol, or nitroglycerol and acids together, should be set on a slight incline, so that they may be drained thoroughly on emptying them.

No more nitroglycerol should be made in one plant in a day than can be handled by two men working in a combined nitrating and separating house as described above. If more is to be handled, even occasionally, it will pay to have another plant entirely separate. The second plant is very valuable in case of emergencies, either due to explosions or the necessity for repairs to the apparatus.

The quality of the mixed acids and glycerol used must be given careful attention, and both should be bought under specifications embodying the analytical method. The method given by Lunge for the analysis of the acids is best for this purpose, while that given in this Journal, 17, 277, was devised by the author especially for such use in the case of glycerol. The strict enforcement of such specifications has led to the saving of at least \$5,000 in a single year in the case of a factory turning out 9,000 or 10,000 pounds of dynamite per day.

The mixing of the nitroglycerol with the absorbent may be conducted in a building on the same level as the storehouse for that explosive. The best form of mixing machine now in use, is practically the well-known wheel-mill of the powder manufacturer. It consists of a circular wooden trough capable of containing a mixing of 500 pounds of dynamite at a time. In this trough, two large wooden wheels run, each followed by a brass plough which has a strip of rubber fastened at the lower edge, thus cleaning the trough without requiring an actual contact. Such an apparatus requires less time for mixing than the old method of using rakes, and is more thorough. The only danger is from nails, or other foreign substances getting into the trough, and to avoid this the absorbent should always be sifted. This is done best before the different ingredients are put together. The nitroglycerol should be brought from the storehouse in a small lead-lined tank, placed on wheels, and arranged as a push-cart. This is wheeled upon scales set in the floor of the storehouse, counterbalanced, and the required amount of nitroglycerol for one mix, run into it through an opening in the top. It is then wheeled along a platform to the mix-house.

This platform should have guides to prevent the cart from running off. At the mix-house, the nitroglycerol flows from the tank into the mixing trough through a piece of rubber hose attached to a small spigot in the bottom of the tank. The end of this hose is securely fastened to the top of the tank during the weighing and transportation of the nitroglycerol. This plan for transporting the explosive is superior to any of the old methods using pails, since they, even at the best, require some handling, with the consequent danger of dropping. The danger of spilling is also reduced to a minimum by this method.

The dynamite next passes to the pack-houses, where it is packed in paper cartridges of almost any desired size. Many packing machines are in use, but the old method of filling the cartridge by placing the open end over the tube of a tin funnel, and pressing the dynamite into place with a wooden packing stick, is preferable on the score of safety. From the pack-house the cartridges pass to the casing house, which process presents no particular points of difficulty, and from there to the magazines, or cars, as the case may be.

We now come to the part of the manufacture which is carried on outside the danger limits, and which includes the regaining of the spent acids already described. The arrangement of this part of the plant is solely with regard to convenience, and offers no particular difficulties due to the nature of the work with the possible exception of the storehouse for the sodium nitrate, which should be at a reasonable distance from other buildings, and upon which no water should be thrown in case of fire. The sodium nitrate is best ground and dried in a steam-jacketed pan, in which heavy iron rollers run, as in the wheel-mill before mentioned. Steam-jacketed pans are also provided for the wood-pulp, kieselguhr, etc.

The paper cartridges were formerly made by hand, and a large factory required a considerable number of girls for this purpose; but at least one machine is known to the writer, which does satisfactory work for a considerable range of diameters and lengths by a very simple adjustment.

Besides the examination of the mixed acids and glycerol above mentioned, the chemist should make frequent determinations of the nitroglycerol in the finished product, as a check on the mix-

ing and weighing. The spent and regained acids may be analyzed as a check on the working of the regaining plant, while valuable information is often brought out by an examination of the various absorbents.

MILLVILLE, N. J., APRIL, 1897.

## PROTEID OF THE WHITE PODDED ADZUKI BEAN.<sup>1</sup>

(*Phaseolus Radiatus*).

BY THOMAS B. OSBORNE AND GEORGE F. CAMPBELL.

Received April 12, 1897.

**T**HIS is a small red bean cultivated in Japan. The seeds used in this investigation were grown in Kansas and sent to us by Professor C. C. Georgeson.

As our object was to discover the nature of the globulin forming the chief proteid constituent of various leguminous seeds, no attempt was made to determine the total amount of proteid contained in this seed, nor to study the other proteid substances occurring in small quantity.

It was impossible, by any means at our command, to remove the closely adhering red seed-coat, but as it was found that this yielded but little coloring matter to salt solution the entire seed was ground until all passed a sieve of fine bolting cloth.

Two kilograms of this meal were treated with eight liters of ten per cent. sodium chloride solution, and after stirring some time the mixture was strained on fine bolting cloth.

After standing long enough to deposit most of the suspended starch the extract was filtered quite clear and saturated with ammonium sulphate. The precipitate so produced was filtered out, suspended in water, and in order to remove the adherent ammonium sulphate, which prevented solution of the proteid in a sufficiently small volume of water, the mixture was dialyzed over night. The proteid was thus completely dissolved. The solution was filtered perfectly clear and again dialyzed four days. A large precipitate of globulin resulted, which was filtered out and a portion collected on a separate paper and washed thoroughly with water and alcohol and dried over sulphuric acid. This was found to weigh 13.21 grams and formed preparation 1.

<sup>1</sup> From the Report of the Connecticut Agricultural Experiment Station for 1896.

The remainder of the globulin was suspended in 850 cc. of water and 150 cc. of ten per cent. salt solution added, which yielded a nearly clear solution, showing the globulin to be readily soluble in one and a half per cent. brine. The solution was filtered clear and the filter washed with 100 cc. of one and a half per cent. salt solution. The filtered liquid, measuring 1100 cc., was treated with 500 cc. of water, thereby throwing down a large rapidly settling precipitate, which, after decanting the fluid, was dissolved in ten per cent. salt solution, filtered perfectly clear and dialyzed for three days. The globulin was thus nearly completely precipitated, for further dialysis of the filtered solution caused separation of very little more. Under the microscope the globulin appeared as well developed spheroids. After filtering this precipitate was washed with water and with alcohol and dried over sulphuric acid. This formed preparation 2, weighing 41.5 grams.

The solution decanted from the first precipitation of 2, caused by the addition of 500 cc. of water as described above, was further diluted with 500 cc. of water, which caused an abundant separation of proteid. After settling over night the clear solution was decanted from the precipitate and the latter washed thoroughly with water and with alcohol and dried over sulphuric acid, giving preparation 3, weighing 31.34 grams.

The solution decanted from 3 was cooled over night in an ice chest to 9°, which caused a further separation of proteid in large spheroids. This was filtered off, washed with water and alcohol, dried over sulphuric acid and found to weigh 6.18 grams, preparation 4.

The filtrate from 4 was dialyzed for twenty-four hours and filtered from an abundant precipitate. The latter was washed with water and alcohol, and after drying weighed 12.0 grams, preparation 5. The filtrate from 5 gave only a trace of precipitate on further dialysis.

The preparations were dried to constant weight at 110° and analyzed. The following figures show that fractional precipitation had caused no separation and that the globulin is identical in composition with phaseolin as obtained from the white bean, *Phaseolus vulgaris*.<sup>1</sup>

<sup>1</sup> This Journal, 16, 633.

## PHASEOLIN.

## Adzuki Bean.

	1	2	3	4	5
Carbon .....	52.31	52.56	52.74	52.74	52.44
Hydrogen .....	7.03	6.98	6.94	6.97	6.91
Nitrogen .....	16.43	16.41	16.34	16.62	16.47
Sulphur .....	0.57	0.62	0.56	0.49	0.61
Oxygen .....	23.66	23.43	23.42	23.18	23.57
	<hr/>	<hr/>	<hr/>	<hr/>	<hr/>
	100.00	100.00	100.00	100.00	100.00
Ash .....	0.16	0.73	0.32	0.90	0.05

Average  
Adzuki bean.

52.56  
6.97  
16.45  
0.57  
23.45  

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100.00

Average  
White bean.

52.58  
6.84  
16.47  
0.56  
23.55  

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100.00

The reactions of phaseolin, whether obtained from the common white bean or the adzuki, are as follows :

In cold and warm water it is entirely insoluble.

In sodium chloride solutions it is readily soluble, one per cent. brine dissolving large quantities of phaseolin.

In dilute acids and alkalies it is readily soluble ; the solutions are precipitated by neutralization.

Solutions in dilute nitric or acetic acid are not precipitated even by large excess of acid.

Dissolved in one-fourth per cent. sodium carbonate solution, phaseolin is precipitated by neutralization, the precipitate being wholly dissolved on adding sodium chloride.

Phaseolin dissolved in ten per cent. sodium chloride brine reacts as follows: It is *not* precipitated even by large excess of hydrochloric, nitric, sulphuric or acetic acids. By a large quantity of trichloroacetic acid a precipitate is produced. By dilution with a sufficient quantity of water a precipitate results. Saturation with sodium chloride or magnesium sulphate does not precipitate the phaseolin, but saturation with ammonium sulphate completely throws it out of solution, while saturation with sodium sulphate at 34° precipitates it mostly, but not entirely. Potassium ferrocyanide together with a large excess of acetic acid gives a precipitate.

With mercuric chloride dissolved in ten per cent. salt solution, no precipitate is produced. With tannin large precipitates result. With picric acid dissolved in ten per cent. salt solution, no precipitate forms until a considerable quantity of the acid is added, and the precipitate thus produced dissolves on adding salt solution.

Phaseolin gives with the biuret, Adamkiewics', Millon', and xanthoproteic tests, the usual proteid reactions.

When solutions in ten per cent. sodium chloride brine are heated, turbidity occurs between 90° and 95° and a small flocculent coagulum separates at 97° to 98°; even prolonged heating in the boiling water-bath coagulates but a small part of this globulin.

The solution, filtered from globulin which had separated on dialyzing the solution of the proteids precipitated by saturating the seed extract with ammonium sulphate, was again saturated with this salt, and the precipitate thereby produced was dissolved in a small volume of water, and after filtering clear, the solution was dialyzed for six days. Three grams of a dark-colored globulin separated which seemed much contaminated with coloring matter. This was filtered out and the clear filtrate dialyzed five days longer, but no precipitate was obtained. The solution was then dialyzed into alcohol and the precipitate which resulted after drying weighed eight and a half grams. The filtrate contained but a trace of proteid. This substance was ground to a powder, thoroughly exhausted with water, washed with alcohol, dried and found to weigh 7.05 grams. Dried at 110° this preparation, 6, had the following composition, which it will be noticed is similar to that of preparations obtained in a like manner from the pea, vetch and cow pea.

Adzuki bean. 6	5	Pea. 8	Vetch 20	8	Cow pea. 9
53.97	53.33	53.54	53.55	53.13	53.36
7.01	6.98	6.99	6.70	7.09	7.05
16.31	16.14	16.69	16.46	16.51	16.21
0.88	1.00	1.01	1.02	1.09	1.13
21.83	22.55	21.77	22.27	22.18	22.25
<hr/> 100.00	<hr/> 100.00	<hr/> 100.00	<hr/> 100.00	<hr/> 100.00	<hr/> 100.00

Preparation 8 from the cow pea was obtained by prolonged dialysis in water, and accordingly must be regarded as a very



soluble globulin. Since preparations agreeing well in composition and general properties with it have been similarly obtained from other leguminous seeds by dialysis, it is our opinion that the above analyses represent a distinct globulin which can be only in part removed from its solutions by dialysis in water, but is wholly separated, in a coagulated form, by dialysis in alcohol. This globulin is at present being further investigated, and it is our intention to offer more respecting its properties in a subsequent paper.

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#### NOTE.

*The Electrolytic Determination of Cadmium.*<sup>1</sup>—In preparing this paper we overlooked the paragraph on cadmium in Dr. Warwick's article, "Die Elektrolyse von Metall-Formiaten."<sup>2</sup> We are under obligations to Prof. Edgar F. Smith for calling attention to this oversight. S. AVERY and BENTON DALES.

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A Detailed Course of Qualitative Chemical Analysis of Inorganic Substances, with Explanatory Notes. By Arthur A. Noyes, Ph.D., Assistant Professor of Chemistry in the Massachusetts Institute of Technology. Third Revised and Enlarged Edition. 89 pp. 1897. New York: The Macmillan Co. Price, \$1.25.

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<sup>1</sup> This Journal, 19, 379.

<sup>2</sup> *Ztschr. anorg. Chem.*, 1, 291.

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